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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Isao MOCHIDA et al.

Title: EXHAUST GAS TREATING SYSTEMS

Prior Appl. 09/219,870

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Examiner: Not yet assigned

Art Unit: Not yet assigned

DIVISIONAL PATENT APPLICATION TRANSMITTAL

Assistant Commissioner for Patents
Box PATENT APPLICATION
Washington, D.C. 20231

Sir:

Transmitted herewith for filing under 37 C.F.R. § 1.53(b) is a:

[ ] Continuation [X] Divisional [ ] Continuation-In-Part (CIP)

of the above-identified copending prior application in which no patenting, abandonment, or termination of proceedings has occurred. Priority to the above-identified prior application is hereby claimed under 35 U.S.C. § 120 for this divisional application. The entire disclosure of the above-identified prior application is considered as being part of the disclosure of the accompanying divisional application and is hereby incorporated by reference therein.

Enclosed are:

[X] Specification, Claim(s), and Abstract (42 pages).

[X] Formal drawings (17 sheets, Figures 1-18).

[X] Declaration and Power of Attorney (5 pages).

[X] Preliminary Amendment (3 pages).

002.377534.1

[X] Information Disclosure Statement (2 pages).

[X] Form PTO-1449 (1 page).

The filing fee is calculated below:

	Claims as Filed		Included in Basic Fee		Extra Claims		Rate		Fee Totals
Basic Fee							$690.00		$690.00
Total Claims:	5	-	20	=	0	x	$18.00	=	$0.00
Independents:	2	-	3	=	0	x	$78.00	=	$0.00
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[X] The Assistant Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 C.F.R. §§ 1.16-1.17, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by a check being in the wrong amount, unsigned, post-dated, otherwise improper or informal or even entirely missing, the Assistant Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741.

Please direct all correspondence to the undersigned attorney or agent at the address indicated below.

Respectfully submitted,

Date **August 21, 2000**

By [signature]

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No. 080542/0151

In re patent application of

Isao MOCHIDA et al.

Serial No. Unassigned

Group Art Unit: Unassigned

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For: HEAT-TREATED ACTIVE CARBONS FOR USE IN DENITRATION, PROCESSES FOR PRODUCING SAME, DENITRATION METHOD USING SAME, AND DENITRATION SYSTEM USING SAME

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination on the merits please amend the application as follows:

IN THE CLAIMS:

Please cancel claims 1-5 and 8-19 without prejudice or disclaimer.

Please amend the claims as follows:

6. (Amended) A desulfurization process which comprises bringing a gas containing SO_2, water, and oxygen into contact with a heat-treated active carbon fiber for use in desulfurization [as claimed in any one of claims 2 to 4] wherein said heat-treated active carbon fiber has been obtained by heat-treating a starting active carbon in a non-oxidizing atmosphere, wherein said starting active carbon is a starting active carbon fiber.

7. (Amended) A high depth desulfurization process which comprises removing sulfur oxides by using a heat-treated active carbon fiber for use in desulfurization, wherein said heat-treated active carbon fiber has been obtained by heat-treating a starting active carbon in a non-oxidizing atmosphere, wherein said heat-treating comprises heating at a temperature of 600 to 1,200° C in a non-oxidizing atmosphere [as

claimed in claim 3 or 4], on the downstream side of a desulfurization apparatus based on the lime-gypsum method.

Please add the following new claims:

--20. The process of claim 6, wherein said heat-treating comprises heating at a temperature of 600 to 1,200° C in a non-oxidizing atmosphere.

21. The process of claim 6, wherein said starting active carbon fiber is a polyacrylonitrile-based or pitch-based starting active carbon fiber.

22. The process of claim 7, wherein said starting active carbon fiber is a polyacrylonitrile-based or pitch-based starting active carbon fiber.--

REMARKS

Entry of the foregoing amendment prior to examination is respectfully requested. This preliminary amendment cancels claims which have been prosecuted in co-pending application 09/219,870, set to issue on August 22, 2000 as U.S. Patent No. 6,106,791 and cancels claims that are presented in a co-pending divisional application filed concurrently. Claims 6 and 7 have been amended to incorporate the subject matter of canceled claim 2 and 3, respectively. New claims 20-22 have been added to incorporate the subject matter of original multiple dependent claims 6 and 7.

An early action on the merits is requested. Should there be any questions, the Examiner is courteously invited to contact the undersigned attorney at the telephone number shown below.

Respectfully submitted,

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Date

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002.375759.1

DESCRIPTION

EXHAUST GAS TREATING SYSTEMS

Technical Field

This invention relates to exhaust gas treating systems for the removal of nitrogen oxides (NO_x) and sulfur oxides (SO_x) present in exhaust gas discharged from boilers, gas turbines, engines and combustion furnaces for burning various types of fuel.

This invention can also be suitably used for the removal of nitrogen oxides present in tunnels and for the removal of nitrogen oxides present in exhaust gas from nitric acid production plants.

Background Art

An example of exhaust gas treatment by means of a conventional exhaust gas treating system is explained with reference to FIG. 1.

In FIG. 1, reference numeral 1 designates a boiler; 2, a denitrator; 3, an air preheater; 4, a dust collector; 5, a gas-gas heater; 6, a desulfurizer; and 7, a stack.

As shown in FIG. 1, a denitrator 2 using a catalyst is installed at the outlet of a boiler 1 or the like, and an air preheater 3 is installed at the outlet of denitrator 2 so as to lower the temperature of the exhaust gas to about 130°C.

The exhaust gas having passed through the aforesaid air preheater 3 is dedusted in a dust precipitator 4, passed

through a gas-gas heater 5 and then introduced into a desulfurizer 6 where sulfur oxides (SO_x) are removed therefrom. Thereafter, the exhaust gas is discharged into the atmosphere through a stack 7.

In order to remove sulfur oxides (SO_x) from exhaust in the aforesaid desulfurizer 6, there has conventionally been employed the so-called lime-gypsum method in which the aforesaid sulfur oxides (SO_x) are absorbed with the aid of calcium carbonate used as absorbing agent and recovered in the form of gypsum. In this method, attempts have been made to reduce the outlet concentration of sulfur oxides (SO_x) by varying the gas-fluid ratio, the residence time and the like.

Usually, the concentration of sulfur oxides (SO_x) in exhaust gas from boilers is in the range of 400 to 800 ppm, and it is intended in the aforesaid lime-gypsum method to reduce the outlet concentration thereof to 50-100 ppm.

However, recent environmental standards demand that the concentration of sulfur oxides (SO_x) in exhaust gas should be reduced to a level of 5 ppm or less which is commonly known as a high-degree desulfurization level. In order to remove sulfur oxides (SO_x) to a level of 50 to 100 ppm according to the aforesaid conventional lime-gypsum method, a marked increase in cost due to an increased size of equipment and the like is unavoidable, even though the conditions are optimized. Moreover, it is desired from the viewpoint of

Thirdly, since the current leak level of NO_x is from 5 to 40 ppm, an excess of NH_3 needs to be injected for the purpose of reducing the leak level of NO_x to zero.

Moreover, recent environmental standards demand that the concentration of nitrogen oxides (NO_x) in exhaust gas should be reduced to a level of 1 ppm or less which is commonly known as a high-degree denitration level. In the aforesaid conventional denitration treatment based on the selective catalytic reduction (SCR) method, a marked increase in cost due to an increased size of equipment and the like is unavoidable, even though the conditions are optimized. On the other hand, it is desired from the viewpoint of environmental problems to improve the efficiency of removal of nitrogen oxides (NO_x).

In view of the above-described problems, an object of the present invention is to provide an exhaust gas treating system which can treat exhaust gas at low temperatures without requiring any heating means and, moreover, can treat exhaust gas efficiently without using a large amount of absorbing agent.

Disclosure of the Invention

In view of the above-described problems of the prior art, the present inventors have made intensive investigations and have now found that an active carbon having been subjected to a specific heat treatment functions as an effective catalyst

for desulfurization or denitration reactions. The present invention has been completed on the basis of this finding.

Accordingly, the present invention relates to a heat-treated active carbon for use in desulfurization or denitration reactions and a desulfurization or denitration process using it.

First of all, the present invention is described below in terms of desulfurization.

The present invention provides a heat-treated active carbon for use in desulfurization reactions which has been obtained by heat-treating a starting active carbon in a non-oxidizing atmosphere.

The present invention also provides a desulfurization process which comprises bringing a gas containing SO_2, water and oxygen into contact with such a heat-treated active carbon for use in desulfurization reactions.

No particular limitation is placed on the type of the starting active carbon. For example, an active carbon fiber or an particulate active carbon is used. Active carbon fibers include those derived from pitch, polyacrylonitrile, phenol, cellulose and the like may be used. Commercial products may also be used. Among others, active carbon having highly hydrophobic surfaces are especially preferred. Specific examples thereof include pitch-based and polyacrylonitrile-based starting active carbon fibers.

The above-described starting active carbon is heat-treated in a non-oxidizing atmosphere. The term "non-oxidizing atmosphere" as used herein comprehends inert gases and reducing atmospheres. No particular limitation is placed on the type of the non-oxidizing atmosphere, so long as the starting active carbon is not oxidized thereby. In particular, inert gases such as nitrogen gas, argon gas and helium gas are preferred. Among them, nitrogen gas is especially preferred because it is readily available.

The heat-treating temperature may be any temperature that renders the surfaces of the starting active carbon hydrophobic. Although the heat-treating temperature may be suitably determined according to the type of the starting active carbon and the like, it is usually in the range of about 600 to 1,200°C. The heat-treating time may be suitably determined according to the heat-treating temperature and the like. This heat treatment makes it possible to obtain the heat-treated active carbon for use in desulfurization reactions according to the present invention. In the heat-treated active carbon for use in desulfurization reactions according to the present invention, all or part of the hydrophilic oxygen-containing functional groups have been removed in the form of CO, CO_2 and the like as a result of the heat treatment, so that its surfaces are highly hydrophobic as compared with those before heat treatment.

Consequently, the adsorption of SO_2 to SO_2 oxidation sites occurs easily and, moreover, the discharge of the resulting sulfuric acid proceeds rapidly. Thus, it can perform a catalytic function for desulfurization reactions without hindrance.

The desulfurization process of the present invention comprises the step of bringing a gas containing sulfur dioxide (SO_2) into contact with the aforesaid heat-treated active carbon. In this case, the aforesaid gas needs to contain water and oxygen. Although the SO_2 concentration can be suitably regulated, efficient desulfurization can be achieved especially at SO_2 concentrations of about 20 to 500 ppm.

Exhaust gas can be desulfurized in one step by using the heat-treated active carbon of the present invention. Alternatively, the present invention may also be practiced in the form of a high-degree desulfurization process in which the aforesaid heat-treated active carbon for the treatment of exhaust gas is used to remove sulfur oxides on the downstream side of a desulfurization apparatus based on the lime-gypsum method.

It is desirable that the aforesaid gas contains water at a relative humidity of 100% or greater and oxygen in an amount of 3% by volume or more (preferably 3 to 21% by volume). Any gaseous components other than those described above may be

present therein, provided that they do not interfere with desulfurization reactions significantly. For example, nitrogen, carbon dioxide, carbon monoxide and the like may be present therein.

Although the contact temperature can be suitably changed according to the type of the heat-treated active carbon, the SO_2 concentration and the like, it may usually be in the range of about 20 to 100°C. Especially in the process of the present invention, efficient desulfurization can be achieved at ordinary temperatures (i.e., about 20 to 50°C). Even at high temperatures above 100°C, desulfurization reactions can be made to proceed by controlling the water content and the like.

The flow rate of the aforesaid gas can be suitably changed according to the SO_2 concentration, the type of the apparatus, and the like. However, it may usually be in the range of about 1×10^{-3} to 5×10^{-3} g·min/ml per unit weight of the active carbon.

In the process of the present invention, any well-known reactors may be used. For example, various types of reactors such as fixed-bed flow reactors, fluidized-bed reactors and stirred reactors may be used.

The resulting sulfuric acid may be recovered according to various recovery methods including, for example, (a) the method of absorbing the sulfuric acid into water to recover

it as concentrated sulfuric acid, (b) the method of absorbing the sulfuric acid into an aqueous solution of KOH to recover it as a neutralized solution, (c) the method of neutralizing the sulfuric acid with an aqueous solution of $Ca(OH)_2$, $Mg(OH)_2$ or the like to recover it as a salt, and (d) the method of absorbing the sulfuric acid into aqueous ammonia to recover it as a fertilizer (i.e., ammonium sulfate).

Similarly to the above-described heat-treated active carbon for use in desulfurization, a heat-treated active carbon for use in denitration can also be obtained by heat-treating a starting active carbon at a temperature of about 600 to 1,000°C in a non-oxidizing atmosphere. The type of the atmosphere and other conditions may be the same as described above.

A first process of the present invention for removing nitrogen oxides by means of a heat-treated active carbon for use in denitration comprises providing a nitrogen oxide oxidation tower packed with a heat-treated active carbon for use in denitration which has been obtained by heat-treating a starting active carbon at a temperature of 600 to 1,000°C, and passing exhaust gas through the oxidation tower to oxidize and remove nitrogen oxides (NO_x) present therein.

A second process of the present invention for removing nitrogen oxides by means of a heat-treated active carbon for use in denitration comprises providing a plurality of

adsorption towers packed with a heat-treated active carbon for use in denitration which has been obtained by heat-treating a starting active carbon at a temperature of 600 to 1,000°C, the adsorption towers being arranged in parallel; and passing exhaust gas successively through the adsorption towers in such a way that the exhaust gas is switched from one adsorption tower to another before a breakthrough of the nitrogen dioxide (NO_2) adsorbed on the heat-treated active carbon for use in denitration within the one adsorption tower occurs, and nitrogen oxides (NO_x) present in the exhaust gas are thereby oxidized, adsorbed and removed continuously.

Moreover, in a high-degree denitration process in accordance with the present invention, nitrogen oxides can be removed by using a heat-treated active carbon for use in denitration, on the downstream side of a denitration treatment based on the selective catalytic reduction (SCR) method.

In the aforesaid processes for the removal of nitrogen oxides, it is preferable to treat the exhaust gas at a temperature of as low as 150°C or below.

In the aforesaid processes for the removal of nitrogen oxides, the nitrogen oxides oxidized by the heat-treated active carbon for use in denitration can be continuously absorbed into an absorbing fluid such as water or an aqueous alkaline solution, and recovered as nitric acid or a salt

thereof.

In the aforesaid processes for the removal of nitrogen oxides, no particular limitation is placed on the type of the starting active carbon, as is the case with the heat-treated active carbon for use in desulfurization. However, it is desirable to use a polyacrylonitrile-based or pitch-based starting active carbon fiber as the starting active carbon fiber.

According to the present invention, the desulfurization performance of a starting active carbon can be improved by heat-treating it in a non-oxidizing atmosphere. The principle thereof is illustrated in FIG. 2.

Prior to heat treatment, the surface of the starting active carbon has many oxygen-containing functional groups distributed thereover as shown in FIG. 2(a), and hence exhibits hydrophilicity. In this case, surface water hinders SO_2 from being adsorbed to SO_2 oxidation sites. Moreover, sulfuric acid formed by oxidation and hydration is captured by surface water and accumulated on the surface of the starting active carbon, thus hindering desulfurization reactions from proceeding smoothly.

In contrast, hydrophilic oxygen-containing functional groups have been removed, in the form of CO, CO_2 and the like, from the surface of the heat-treated active carbon, as shown in FIG. 2(b). Thus, its surface exhibits

hydrophobicity. Consequently, SO_2 is readily adsorbed to SO_2 oxidation sites and, moreover, the resulting sulfuric acid is eliminated rapidly, so that the heat-treated active carbon of the present invention exhibits a high activity for desulfurization reactions without being hindered by sulfuric acid.

In order to remove sulfur oxides (SO_x) present in exhaust gas by means of a heat-treated active carbon as described above, the exhaust gas is conditioned so as to have a temperature of 100°C or below, preferably 50°C or below, and a relative humidity of 100% or greater. Thereafter, the exhaust gas is introduced into a reactor packed with the heat-treated active carbon where sulfur oxides (SO_x) present therein are oxidized to sulfur trioxide (SO_3) at the surfaces of the heat-treated active carbon. Then, this sulfur trioxide (SO_3) is reacted with water or an aqueous solution of sodium hydroxide or the like to recover it as sulfuric acid or a salt thereof. Thus, sulfur oxides (SO_x) present in exhaust gas can be removed.

Ordinary active carbon have the property of adsorbing nitrogen monoxide (NO), but fail to exhibit sufficient oxidizing power. Although some of them have oxidizing power, their surface structure makes it difficult to remove nitrogen oxides in the form of nitrogen dioxide (NO_2).

The reason for this is that plenty of oxygen-containing

groups (such as carbonyl and carboxyl groups) and N- or S-containing groups remain on the surface of such active carbon.

According to the present invention, a starting active carbon is heat-treated in a non-oxidizing atmosphere. This decomposes and eliminates various groups present on the surfaces of the starting active carbon to activate NO oxidation sites. Moreover, hydrophilic oxygen-containing functional groups are also decomposed to decrease water (H_2O) adsorption sites which hinder the adsorption of NO and the elimination of NO_2. Thus, an improvement in NO-oxidizing activity can be achieved.

When an active carbon which has been heat-treated in this manner is used, nitrogen monoxide (NO) present in exhaust gas is adsorbed thereon, and then oxidized by O_2 to form nitrogen dioxide (NO_2).

This nitrogen dioxide (NO_2) may be removed in the state adsorbed on the active carbon. Alternatively, the desorbed nitrogen dioxide (NO_2) may be absorbed into water and recovered in the form of an aqueous solution of nitric acid, or may be absorbed into an aqueous alkaline solution and recovered in the form a salt of nitric acid. Thus, exhaust gas can be denitrated in the above-described manner.

As described above, the present invention makes it possible to remove nitrogen oxides and sulfur oxides from

exhaust gas at a low temperature of 150°C or below by using a heat-treated active carbon.

Accordingly, a system in accordance with the present invention may be used as a substitute for the currently used denitrators and desulfurizers. Alternatively, when it is desired to improve the denitration or desulfurization performance of the current system, a system in accordance with the present invention may be connected therewith to achieve a further improvement in treating capacity.

Moreover, the desulfurization processes of the present invention using a heat-treated carbon for use in desulfurization reactions make it possible to desulfurize exhaust gas efficiently without using a large volume of water (i.e., in a dry manner). Especially when a heat-treated pitch-based carbon fiber for use in desulfurization reactions is used, the degree of removal of SO_2 may be raised to 100% depending on the temperature used for the heat treatment.

Furthermore, as shown in FIG. 18, the SO_2 adsorbed on the surface of a heat-treated active carbon for use in desulfurization reactions according to the present invention is oxidized by O_2 present in the gas to form SO_3, and the latter reacts with water present in the gas to form sulfuric acid. Then, this sulfuring acid is washed away from the surface. That is, by treating sulfur oxides-containing exhaust gas with a heat-treated active carbon, the

concentration of sulfur oxides (SO_x) in the exhaust gas can be reduced to a level of 5 ppm or less which has been difficult to achieve in the prior art, and such sulfur oxides can be recovered in the form of sulfuric acid (in particular, concentrated sulfuric acid).

Furthermore, according to the present invention, the nitrogen oxides oxidized on a heat-treated active carbon can be continuously treated by converting them into nitric acid or a salt thereof in an absorption tower. In addition, by carrying out high-degree denitration using a heat-treated active carbon in combination with conventional denitration based on selective catalytic reduction using a V_2O_5 catalyst, the concentration of nitrogen oxides (NO_x) in exhaust gas can be reduced to a level of 1 ppm or less which has been difficult to achieve in the prior art.

The heat-treated active carbon for use in desulfurization reactions and the desulfurization processes, and the heat-treated active carbon for use in denitration reactions and the denitration processes, which are provided by the present invention, may be suitably used for the removal of sulfur oxides and nitrogen oxides produced in combustion equipment (such as boilers and thermal electric power plants) especially for burning heavy oil, coal and the like, sulfuric acid production plants, nitric acid production plants, metal processing works and facilities, paper mills, and tunnels.

Brief Description of the Drawings

FIG. 1 is a block diagram of a conventional exhaust gas treating system;

FIGs. 2(a) and 2(b) are schematic views showing the surface states of an active carbon before high-temperature treatment and an active carbon in accordance with the present invention, respectively;

FIG. 3 is a graph showing the relationship between the heat-treating temperature of a pitch-based carbon fiber or a particulate active carbon and the degree of desulfurization;

FIG. 4 is a graph showing the relationship between the heat-treating temperature of a polyacrylonitrile (PAN)-based carbon fiber and the degree of desulfurization;

FIG. 5 is a block diagram of an exemplary system for carrying out the high-degree desulfurization process of the present invention;

FIG. 6 is a graph showing the relationship between the concentrations of nitrogen oxides and the time of reaction with an active carbon fiber;

FIG. 7 is a graph showing the relationship between the heat-treating temperature of a pitch-based carbon fiber or a particulate active carbon and the degree of denitration;

FIG. 8 is a graph showing the relationship between the heat-treating temperature of a polyacrylonitrile (PAN)-based carbon fiber and the degree of denitration;

FIG. 9 is a block diagram of a system for carrying out the denitration process of the present invention;

FIG. 10 is a schematic view of an exemplary absorption tower in accordance with the present invention;

FIG. 11 is a block diagram of a system for carrying out the denitration process of the present invention;

FIG. 12 is a block diagram of a system for carrying out the denitration process of the present invention;

FIG. 13 is a schematic view illustrating a first embodiment of the exhaust gas treating system in accordance with the present invention;

FIG. 14 is a graph showing the performance on the oxidation of nitrogen monoxide to nitrogen dioxide (NO_2);

FIG. 15 is a graph showing the performance on the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3);

FIG. 16 is a schematic view illustrating a second embodiment of the exhaust gas treating system in accordance with the present invention;

FIG. 17 is a schematic view illustrating a third embodiment of the exhaust gas treating system in accordance with the present invention; and

FIG. 18 is a schematic view showing the manner in which SO_2 is removed on the surface of an active carbon in accordance with the present invention.

Best Mode for Carrying Out the Invention

The features of the present invention are more specifically described hereinbelow with reference to the following examples and comparative examples.

Example 1

A pitch-based starting active carbon ("OG-20A"; manufactured by Osaka Gas Co., Ltd.) and a starting particulate active carbon ("HC-30"; manufactured by Turumicoal Co.,Ltd) were used as the starting active carbon fiber. A series of heat-treated active carbon were obtained by firing the starting active carbon at various temperatures ranging from 400 to 1,400°C in an atmosphere of nitrogen for an hour.

Then, each of the heat-treated active carbon thus obtained was used in a desulfurization reaction to examine the desulfurization performance thereof. In this desulfurization reaction, a gas composed of 1,000 ppm of SO_2, 5 vol.% of O_2, 10 vol.% of water and the balance N_2 was used. Using a fixed-bed flow reactor, the aforesaid gas was passed therethrough at a temperature of 30°C in an amount of 1.0 g·min/ml per unit weight of the active carbon. The SO_2 concentration in the gas emerging from the outlet of the reactor was measured with a gas chromatograph having a FPD detector, and the degree of SO_2 removal was calculated. The results obtained 15 hours after the start of the desulfurization reaction are shown in FIG. 3.

As shown in FIG. 3, their activities vary according to the heat-treating temperature.

Thus, heat-treating temperatures in the range of 600 to 1,200°C have been judged to be effective. In the present invention, therefore, an active carbon heat-treated at a temperature in this range is used to enhance the catalytic activity for the oxidation of sulfur dioxide (SO_2) and sulfur trioxide (SO_3) and treat them without being influenced by other coexisting gases such as CO and CO_2.

As a result, it has been become possible to remove low concentrations of sulfur dioxide (SO_2) and sulfur trioxide (SO_3).

Comparative Example 1

A desulfurization reaction was carried out in the same manner as described in Example 1, except that the aforesaid pitch-based active carbon fiber was used without being fired. Thus, the degree of SO_2 removal was calculated. As a result, the degree of SO_2 removal was found to be as low as 20%, indicating that SO_2 could not be fully removed.

Example 2

A polyacrylonitrile-based active carbon fiber ("FE-300"; manufactured by Toho Rayon Co., Ltd.) was used as the starting active carbon fiber. This active carbon fiber was heat-treated in the same manner as described in Example 1. Then, each of the heat-treated active carbon fibers was used

in a desulfurization reaction and the degree of SO_2 removal was calculated. The results thus obtained are shown in FIG. 4.

Again, their activities vary according to the heat-treating temperature. Thus, heat-treating temperatures in the range of 600 to 1200°C have been judged to be effective. In the present invention, therefore, an active carbon fiber heat-treated at a temperature in this range is used to remove sulfur dioxide (SO_2) and sulfur trioxide (SO_3).

Example 3

FIG. 5 illustrates an exhaust gas desulfurization system in accordance with one embodiment of the present invention.

In FIG. 5, reference numeral 11 designates a boiler; 12, a denitrator; 13, an air preheater; 14, a dust collector; 15, a gas-gas heater; 16, a desulfurizer; 17, a stack; and 18, a high-degree desulfurizer.

As shown in FIG. 5, exhaust gas discharged from a boiler 11 is passed through a denitrator 12 and a desulfurizer 16 where nitrogen oxides (NO_x) and sulfur oxides (SO_x) are removed therefrom in the same manner as in the prior art.

Thereafter, the exhaust gas is introduced into a high-degree desulfurizer 18 where it is brought into contact with an active carbon fiber heat-treated at a temperature in the range of 600 to 1,200°C and packed into high-degree desulfurizer 18, so that the reactions represented by the

following equations (a) and (b) are promoted. Thus, the concentration of sulfur oxides (SO_x) in the exhaust gas could be reduced to 5 ppm or less.

(a) $SO_2 + 1/2O_2 \longrightarrow SO_3$

(b) $SO_3 + H_2O \longrightarrow H_2SO_4$

The treating conditions employed in this example are given below.

(Treating conditions)

a) Gas to be treated

Temperature: 50°C

Relative humidity: 100% R.H.

SO_x concentration: 120 ppm

Flow rate: 50 m^3/hr

b) Desulfurizer

Active carbon fiber: OG-20A

Amount of catalyst: 0.5 kg

c) Desulfurized gas

SO_x concentration: 5 ppm

In this removal of sulfur oxides (SO_x), the water used in the aforesaid high-degree desulfurizer 18 may be replaced by an aqueous solution of sodium hydroxide or the like. Thus, the sulfur oxides (SO_x) can be recovered as a salt of sulfuric acid (e.g., sodium sulfate) instead of sulfuric acid.

The heat-treated active carbon fiber packed into the

aforesaid high-degree desulfurizer 18 is one obtained by firing a pitch-based starting active carbon fiber (i.e., an active carbon fiber formed by the melt spinning of pitch obtained as residue in coal chemical and petrochemical processes) in a reducing atmosphere.

In this example, there was used a pitch-based active carbon fiber manufactured and sold by Osaka Gas Co., Ltd. under the trade name of "OG-20A". This pitch-derived active carbon fiber was fired at about 1,100°C in a reducing atmosphere for an hour, shaped into a corrugated form, and then used in this example.

Moreover, a polyacrylonitrile (PAN)-based active carbon fiber obtained by firing and carbonizing a high-molecular-weight polyacrylonitrile fiber was also used as the heat-treated active carbon fiber. Thus, the concentration of sulfur oxides (SO_x) in exhaust gas could be reduced to 5 ppm or less in the same manner as described above.

Example 4

A pitch-based starting active carbon fiber ["OG-5A" (trade name); manufactured by Osaka Gas Co., Ltd.] formed by the melt spinning of pitch obtained as residue in coal chemical and petrochemical processes, a polyacrylonitrile-based starting active carbon fiber ["FE-300" (trade name); manufactured by Toho Rayon Co., Ltd.] formed by firing and carbonizing a high-molecular-weight polyacrylonitrile fiber,

and a starting particulate active carbon ["HC-30" (trade name); manufactured by Turumicoal Co., Ltd.] were used as starting active carbon. These starting active carbon were fired at various temperatures ranging from 400 to 1,400°C in an atmosphere of nitrogen for an hour.

Then, the heat-treated active carbon thus obtained were tested for NO-oxidizing activity.

For purposes of comparison, the pitch-based and polyacrylonitrile-based starting active carbon fibers which had not been heat-treated were tested in the same manner.

Specifically, using a fixed-bed flow reactor, a gas composed of 380 ppm of NO, 4.0 vol.% of O_2, 2.5 vol.% of H_2O and the balance N_2 was passed therethrough at a reaction temperature of 25°C in an amount (W/F) of 1.0×10^{-2} g·min/ml.

Using a chemiluminescent NO_x detector, the effluent gas was analyzed for NO and NO_2. Thus, the degree of conversion of NO to NO_2 was evaluated.

When a NO-containing gas is introduced into the pitch-based active carbon fiber, its ability to oxidize and adsorb NO causes the outlet NO_x concentration to be reduced to several tens of parts per million in an initial stage (FIG. 6).

Then, the outlet NO_2 concentration increases as a result of breakthrough of NO_2. After the lapse of 35 hours or more,

a complete breakthrough of NO_2 is observed.

However, the degree of conversion of NO to NO_2 remains substantially constant thereafter, and a steady state is reached 40 hours after the start of the reaction.

FIGs. 7 and 8 show the relationship between the heat-treating temperature for the pitch-based or polyacrylonitrile (PAN)-based active carbon fiber or the particulate active carbon used as the starting active carbon and the degree of denitration in the steady state.

As shown in these figures, their activities vary according to the heat-treating temperature.

Thus, heat-treating temperatures in the range of 600 to 1,000°C have been judged to be effective in the present invention.

Comparative Examples 2 and 3

When the pitch-based starting active carbon fiber (Comparative Example 2) and the PAN-based starting active carbon fiber (Comparative Example 3) were used without being subjected to any heat treatment, the degree of denitration was 18% and 4%, respectively.

Example 5

FIG. 9 illustrates an exemplary system for the removal of nitrogen oxides in accordance with the present invention.

In FIG. 9, reference numerals 21a to 21n designate adsorption towers; 22, nitrogen oxides-containing exhaust

gas; 23, a regenerating inert gas; 24, a nitrogen dioxide absorption tower; 25, switching valves; 26, an exhaust gas line; and 27, a regenerating gas line.

As shown in FIG. 9, two or more adsorption towers 21a, ..., 21n are installed in parallel. Initially, nitrogen oxides-containing exhaust gas 22 is introduced into a first adsorption tower 21a by means of a switching valve 25. Thus, nitrogen oxides are oxidized by and adsorbed on a heat-treated active carbon fiber packed into the aforesaid first adsorption tower 21a.

The heat-treated active carbon fiber packed into the aforesaid first adsorption tower 21a is an active carbon fiber which has been heat-treated at a temperature of 600 to 1,000°C in a non-oxidizing atmosphere. This heat-treated active carbon fiber promotes the reactions represented by the following equations (c), so that nitrogen oxides present in the introduced exhaust gas are reacted therewith and adsorbed thereon in the form of nitrogen dioxide (NO_2).

Before a breakthrough of the nitrogen dioxide (NO_2) formed by the oxidation of nitrogen oxides and adsorbed on the heat-treated active carbon fiber within first adsorption tower 21a occurs, the exhaust gas is successively switched to a second and other adsorption towers 21b, ..., 21n. Thus, the exhaust gas is successively introduced thereinto by way of an exhaust gas line 26 and treated to remove nitrogen oxides therefrom.

The heat-treated active carbon fiber packed in each of the adsorption towers showing the aforesaid breakthrough is regenerated by introducing a regenerating inert gas 23 thereinto and releasing the nitrogen dioxide (NO_2) through a regeneration gas line 27.

In order to absorb the nitrogen dioxide (NO_2) released during the aforesaid regeneration process, the regeneration gas is introduced into an absorption tower 24 installed on the downstream side and containing an absorbing fluid such as water or an aqueous alkaline solution. Thus, the regeneration gas is continuously treated by promoting the reactions represented by the following equations (d).

(c) $NO + 1/2O_2 \longrightarrow NO_2$

$4NO + 3O_2 \longrightarrow 2N_2O_5$

(d) $NO_2 + H_2O \longrightarrow HNO_3$

$N_2O_5 + H_2O \longrightarrow 2HNO_3$

As the means for absorbing the aforesaid nitrogen dioxide (NO_2), there may be used any of various apparatus such as tray towers, packed towers, spray towers and stirred towers.

FIG. 10 illustrates an embodiment in which a packed tower is used as the aforesaid absorption tower.

As shown in FIG. 10, exhaust gas is introduced through an exhaust gas inlet 33 provided at the bottom of an absorption tower 30, and the treated gas (i.e., freed of nitrogen oxides) is discharged from a treated gas outlet 34. An

absorbing fluid such as water is introduced through an absorbing fluid inlet 35 provided above the packed region 31 of absorption tower 30 and distributed by a fluid distributor 32.

Thus, the introduced absorbing fluid flows through a corrosion-resistant porcelain packing material placed in packed region 31 and reacts with nitrogen dioxide (NO_2). Thereafter, the absorbing fluid is continuously withdrawn from an absorbing fluid outlet 36 provided at the bottom of absorption tower 30.

The heat-treated active carbon fiber for use in denitration, which is packed into the aforesaid adsorption towers, is one obtained by firing a pitch-based starting active carbon fiber (i.e., an active carbon fiber formed by the melt spinning of pitch obtained as residue in coal chemical and petrochemical processes) in a reducing atmosphere.

In this example, there was used a pitch-based starting active carbon fiber manufactured and sold by Osaka Gas Co., Ltd. under the trade name of "OG-5A". This pitch-based starting active carbon fiber was fired at about 850°C in a non-oxidizing atmosphere for an hour, shaped into a corrugated form, and then used in this example.

Moreover, a polyacrylonitrile (PAN)-based starting active carbon fiber [e.g., "FE-300" (trade name); manufactured by

Toho Rayon Co., Ltd.] obtained by firing and carbonizing a high-molecular-weight polyacrylonitrile fiber was also used as the starting active carbon fiber. Thus, the concentration of nitrogen oxides (NO_x) in exhaust gas could be reduced in the same manner as described above.

Example 6

FIG. 11 illustrates an embodiment in which the treatment of nitrogen oxides is carried out by means of a NO-oxidizing reactor packed with a heat-treated active carbon fiber.

In FIG. 11, reference numeral 42 designates a NO-oxidizing reactor; 41, nitrogen oxides-containing exhaust gas; and 43, a nitrogen dioxide absorption tower.

In this embodiment, the aforesaid NO-oxidizing reactor 42 is packed with the above-described heat-treated active carbon fiber having oxidizing activity. Thus, the introduced nitrogen oxides-containing exhaust gas 41 is oxidized and then continuously treated in an absorption tower 43.

In the above-described treatment, it is more preferable to treat nitrogen oxides present in exhaust gas continuously at a low temperature of 150°C or below.

When applied to the removal of nitrogen oxides (NO_x) present in exhaust gas discharged from boilers, gas turbines, engines and combustion furnaces for burning various types of fuel, the above-described system for the removal of nitrogen oxides makes it possible to treat such exhaust gas.

Moreover, the present invention is also suitable for the removal of nitrogen oxides present in tunnels and for the removal of nitrogen oxides present in exhaust gas from nitric acid production plants.

Furthermore, similarly to the previously described V_2O_5 catalyst, the heat-treated active carbon fiber has an activity for decomposing nitrogen oxides to nitrogen (N_2) and water vapor (H_2O) on the basis of selective catalytic reduction (SCR) when nitrogen oxides (NO_x) and ammonia (NH_3) coexist. Accordingly, exhaust gas can also be denitrated by supplying an appropriate amount of NH_3, together with the exhaust gas, to the heat-treated active carbon fiber placed in the NO-oxidizing reactor.

<u>Example 7</u>

FIG. 12 illustrates an exemplary system for carrying out the denitration process of the present invention.

In FIG. 12, reference numeral 51 designates a boiler; 52, a denitrator; 53, an air preheater; 54, a dust collector; 55, a gas-gas heater; 56, a desulfurizer; 57, a stack; and 58, a high-degree denitrator.

As shown in FIG. 12, exhaust gas discharged from a boiler 51 is passed through a denitrator 52 and a desulfurizer 56 where nitrogen oxides (NO_x) and sulfur oxides (SO_x) are removed therefrom in the same manner as in the prior art.

Thereafter, the exhaust gas is introduced into a high-

degree denitrator 58 where it is brought into contact with an active carbon fiber heat-treated at a temperature in the range of 600 to 1,000°C and packed into high-degree desulfurizer 58. Thus, the reactions represented by the foregoing equations (c) and (d) are promoted.

Consequently, when exhaust gas having a nitrogen oxide (NO_x) concentration of 400 ppm was treated by means of denitrator 52 and desulfurizer 56 in the same manner as in the prior art and the resulting gas having a NO_x concentration of 40 ppm was further treated by means of the aforesaid high-degree desulfurizer 58, the concentration of nitrogen oxides (NO_x) in the exhaust gas could be reduced to 1 ppm or less.

The treating conditions employed in this example are given below.

(Treating conditions)

a) Gas to be treated

Temperature: 50°C

Relative humidity: 60% R.H.

NO_x concentration: 40 ppm

Flow rate: 50 m^3/hr

b) Denitrator

Active carbon fiber: OG-5A

Amount of catalyst: 8 kg

c) Denitrated gas

NO_x concentration: 1 ppm

In this removal of nitrogen oxides (NO_x), the water used in the aforesaid high-degree denitrator 58 may be replaced by an aqueous solution of sodium hydroxide or the like. Thus, the nitrogen oxides (NO_x) can be recovered as a salt of nitric acid (e.g., sodium nitrate) instead of nitric acid.

The heat-treated active carbon fiber packed into the aforesaid high-degree denitrator 58 is one obtained by firing a pitch-based starting active carbon fiber (i.e., an active carbon fiber formed by the melt spinning of pitch obtained as residue in coal chemical and petrochemical processes) in a reducing atmosphere.

In this example, there was used a pitch-based starting active carbon fiber manufactured and sold by Osaka Gas Co., Ltd. under the trade name of "OG-5A". This pitch-based starting active carbon fiber was fired at about 850°C in a reducing atmosphere for an hour, shaped into a corrugated form, and then used in this example.

Moreover, a polyacrylonitrile (PAN)-based active carbon fiber obtained by firing and carbonizing a high-molecular-weight polyacrylonitrile fiber was also used as the heat-treated active carbon fiber. Thus, the concentration of nitrogen oxides (NO_x) in exhaust gas could be reduced to 1 ppm or less in the same manner as described above.

Example 8

FIG. 13 illustrates a first embodiment of the exhaust gas treating system of the present invention.

In FIG. 13, reference numeral 61 designates a boiler; 62, a dust collector; 63, a gas-gas heater; 64, an oxidation tower; 65, nitric acid tower; and 66, desulfurization tower.

As shown in FIG. 13, a dust collector 62 is installed at the outlet of boiler 61 or the like. Exhaust gas having passed through dust collector 62 is introduced into a gas-gas heater 63 where its temperature is lowered to about 90°C and, moreover, its relative humidity is adjusted to 80% or less and preferably 60% or less. Then, the exhaust gas is introduced into an oxidation tower 64.

This oxidation tower 64 is packed with a heat-treated active carbon fiber in corrugated form, by which nitrogen oxides (NO_x) present in the exhaust gas are oxidized to nitrogen dioxide (NO_2) and dinitrogen pentoxide (N_2O_5) [the above equations (c)]. Then, the exhaust gas containing nitrogen dioxide (NO_2) and dinitrogen pentoxide (N_2O_5) is introduced into nitric acid tower 65 where they are reacted with water to form nitric acid [the above equations (d)]. Thus, nitrogen oxides (NO_x) present in the exhaust gas are removed.

Alternatively, the water used in the aforesaid nitric acid tower 65 may be replaced by an aqueous solution of sodium hydroxide or the like. Thus, the nitrogen oxides (NO_x) can

be recovered as a salt of nitric acid (e.g., sodium nitrate) instead of nitric acid.

Thereafter, the exhaust gas freed of nitrogen oxides (NO_x) is humidified to a relative humidity of 100% or greater in nitric acid tower 65 and then introduced into a desulfurization tower 66 packed with a heat-treated active carbon fiber in corrugated form. In this desulfurization tower 66, sulfur oxides (SO_x) are oxidized to sulfur trioxide (SO_3) [the above equation (a)] and the latter is then reacted with water to form sulfuric acid [the above equation (b)]. Thus, sulfur oxides (SO_x) present in the exhaust gas freed of nitrogen oxides (NO_x) are removed.

Thereafter, the exhaust gas is heated in gas-gas heater 63 and discharged from a stack.

The temperature of the exhaust gas is as low as 100°C or below and preferably 50°C or below.

Also in this removal of sulfur oxides (SO_x), the water used in the aforesaid desulfurization tower 66 may be replaced by an aqueous solution of sodium hydroxide or the like, similarly to the removal of nitrogen oxides (NO_x). Thus, the sulfur oxides (SO_x) can be recovered as a salt of sulfuric acid (e.g., sodium sulfate) instead of sulfuric acid.

In this embodiment, the heat-treated active carbon fibers packed into the aforesaid nitric acid tower 65 and

desulfurization tower 66 are ones obtained by firing a pitch-based starting active carbon fiber in a non-oxidizing atmosphere. More specifically, the heat-treated active carbon fiber used for the treatment of nitrogen oxides (NO_x) in this example is one obtained by firing a pitch-based starting active carbon fiber at about 850°C for an hour and shaping it into a corrugated form, and the heat-treated active carbon fiber used for the treatment of sulfur oxides (SO_x) in this example is one obtained by firing a pitch-based starting active carbon fiber at about 1,100°C for an hour and shaping it into a corrugated form. However, it is to be understood that the present invention is not limited thereto.

FIG. 14 shows the performance on the oxidation of nitrogen monoxide (NO) to nitrogen dioxide (NO_2). As shown in FIG. 14, high performance of 80% or greater can be achieved stably.

FIG. 15 shows the performance on the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3). As shown in FIG. 15, high performance of 95% or greater can be achieved stably.

Example 9

FIG. 16 illustrates a second embodiment of the exhaust gas treating system of the present invention.

As shown in FIG. 16, a denitrator 72 is installed at the outlet of a boiler 71 or the like, and an air preheater 73 is installed at the outlet of denitrator 72 so as to lower the

temperature of exhaust gas to about 130°C.

In this embodiment, exhaust gas is first denitrated by means of a conventional denitrator 72. Thereafter, the high-degree removal of nitrogen oxides (NO_x) present in the exhaust gas and the removal of sulfur oxides (SO_x) present therein are carried out by means of the denitration and desulfurization system of Example 8 using heat-treated active carbon fibers.

As shown in FIG. 16, after exhaust gas is denitrated by means of denitrator 72 based on high-temperature treatment, it is passed through the aforesaid air preheater 73, dedusted in a dust collector 74, and further cooled to about 90°C in a gas-gas heater 75. Thereafter, in the same manner as in the first embodiment, the exhaust gas is treated by means of an oxidation tower 76 packed with a heat-treated active carbon fiber in corrugated form, by which the nitrogen oxides (NO_x) remaining in the exhaust gas are oxidized. Then, the exhaust gas containing nitrogen dioxide (NO_2) and dinitrogen pentoxide (N_2O_5) is introduced into a nitric acid tower 77 where they are reacted with water to form nitric acid. Thus, nitrogen oxides (NO_x) present in exhaust gas are removed.

As described above, this system can be connected with a conventionally used denitrator to achieve a further improvement in denitration performance and hence in treating capacity.

Similarly, this system can also be connected with a system having a conventional desulfurizer to achieve a further improvement in desulfurization performance.

Example 10

FIG. 17 illustrates a third embodiment of the exhaust gas treating system of the present invention.

As shown in FIG. 17, exhaust gas from a boiler 81 is dedusted in a dust collector 84, cooled to about 90°C in a gas-gas heater 85, and then introduced into a cooling tower 88 where it is further cooled to 50°C or below and humidified to a relative humidity of 100% or greater. The resulting low-temperature/high-humidity exhaust gas is introduced into a desulfurization tower 89 packed with a heat-treated active carbon fiber in corrugated form, where sulfur oxides (SO_x) are recovered as sulfuric acid or a salt thereof.

In this embodiment, sulfur oxides (SO_x) are removed by oxidizing them in desulfurization tower 89 and reacting the resulting sulfur trioxide with water to form sulfuric acid.

The exhaust gas freed of sulfur oxides (SO_x) is passed again through gas-gas heater 85 constituting a cooling tower, and thereby heated to about 90°C. Then, it is introduced into a denitration tower 86 packed with a heat-treated active carbon fiber, where nitrogen oxides (NO_x) present in the exhaust gas are oxidized to nitrogen dioxide (NO_2). Thereafter, the nitrogen dioxide (NO_2) is removed as nitric

acid in a nitric acid tower 87.

In this embodiment, the relative humidity of exhaust gas is regulated by cooling the exhaust gas in cooling tower 88 before introducing it into desulfurization tower 89. However, its relative humidity may also be regulated by omitting cooling tower 88 and adding steam to the exhaust gas without cooling it.

CLAIMS

1. A heat-treated active carbon for use in the treatment of exhaust gas which has been obtained by heat-treating a starting active carbon in a non-oxidizing atmosphere.

2. A heat-treated active carbon for use in the treatment of exhaust gas as claimed in claim 1 wherein the starting active carbon is a starting active carbon fiber.

3. A heat-treated active carbon fiber for use in desulfurization which has been obtained by heat-treating a starting active carbon fiber at a temperature of 600 to 1,200°C in a non-oxidizing atmosphere.

4. A heat-treated active carbon fiber for use in desulfurization as claimed in claim 3 wherein the starting active carbon fiber is a polyacrylonitrile-based or pitch-based starting active carbon fiber.

5. A heat-treated active carbon fiber for use in desulfurization as claimed in claim 3 or 4 wherein the non-oxidizing atmosphere is an atmosphere of nitrogen gas.

6. A desulfurization process which comprises bringing a gas containing SO_2, water and oxygen into contact with a heat-treated active carbon fiber for use in desulfurization as claimed in any one of claims 2 to 4.

7. A high-depth desulfurization process which comprises removing sulfur oxides by using a heat-treated active carbon fiber for use in desulfurization as claimed in claim 3 or 4,

on the downstream side of a desulfurization apparatus based on the lime-gypsum method.

8. A heat-treated active carbon fiber for use in denitration which has been obtained by heat-treating a starting active carbon fiber at a temperature of 600 to 1,000°C in a non-oxidizing atmosphere.

9. A heat-treated active carbon fiber for use in denitration as claimed in claim 8 wherein the starting active carbon fiber is a polyacrylonitrile-based or pitch-based starting active carbon fiber.

10. A heat-treated active carbon fiber for use in denitration as claimed in claim 8 or 9 wherein the non-oxidizing atmosphere is an atmosphere of nitrogen gas.

11. A high-degree denitration process which comprises removing nitrogen oxides by using a heat-treated active carbon fiber for use in denitration as claimed in claim 8, on the downstream side of a denitration treatment based on the selective catalytic reduction (SCR) method.

12. A process for removing nitrogen oxides by means of a heat-treated active carbon fiber for use in denitration which comprises providing a nitrogen oxide oxidation tower packed with a heat-treated active carbon fiber for use in denitration as claimed in claim 8, and passing exhaust gas through said oxidation tower to oxidize and remove nitrogen oxides (NO_x) present therein.

13. A process for removing nitrogen oxides by means of a heat-treated active carbon fiber for use in denitration which comprises providing a plurality of adsorption towers packed with a heat-treated active carbon fiber for use in denitration as claimed in claim 8, and passing exhaust gas successively through said adsorption towers in such a way that the exhaust gas is switched from one adsorption tower to another before a breakthrough of the nitrogen dioxide (NO_2) adsorbed on the heat-treated active carbon fiber for use in denitration within said one adsorption tower occurs, and the nitrogen oxides (NO_x) present in the exhaust gas are thereby oxidized, adsorbed and removed continuously.

14. A process for removing nitrogen oxides as claimed in any one of claims 11 to 13 wherein the continuous oxidation of nitrogen oxides within said adsorption tower is carried out by treating the exhaust gas at a temperature of as low as 150°C or below.

15. A process for removing nitrogen oxides as claimed in any one of claims 11 to 13 wherein the nitrogen oxides oxidized by the heat-treated active carbon fiber for use in denitration are continuously absorbed into an absorbing fluid.

16. An exhaust gas treating system wherein exhaust gas containing nitrogen oxides (NO_x) and sulfur oxides (SO_x) is treated with a heat-treated active carbon for use in the

treatment of exhaust gas as claimed in claim 2, so that the nitrogen oxides (NO_x) are recovered as nitric acid or a salt thereof and the sulfur oxides (SO_x) are recovered as sulfuric acid or a salt thereof.

17. An exhaust gas treating system as claimed in claim 16 wherein the temperature of the gas being treated is as low as 100°C or below.

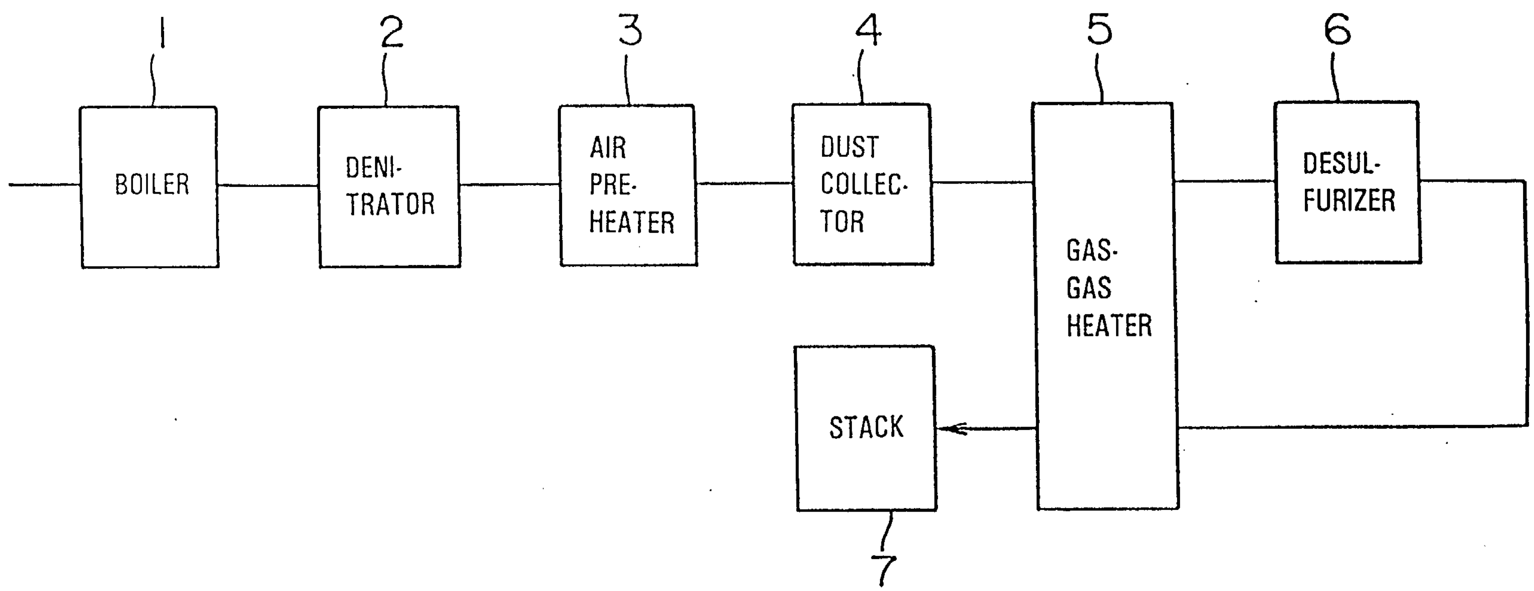
18. An exhaust gas treating system as claimed in claim 16 or 17 wherein the relative humidity of the gas being treated is 80% or less when the nitrogen oxides (NO_x) are recovered as nitric acid or a salt thereof.

19. An exhaust gas treating system as claimed in claim 16 or 17 wherein the relative humidity of the gas being treated is 100% or greater when the sulfur oxides (SO_x) are recovered as sulfuric acid or a salt thereof.

ABSTRACT

An active carbon for use in the treatment of exhaust gas can be obtained by heat-treating a starting active carbon fiber derived from polyacrylonitrile, pitch or the like or a starting particulate active carbon in a non-oxidizing atmosphere. The heat-treating temperature is preferably in the range of 600 to 1,200°C for use in the desulfurization of exhaust gas, and in range of 600 to 1,000°C for use in the denitration of exhaust gas. By using the resulting heat-treated active carbon for the purpose of desulfurization, the sulfur oxide concentration in exhaust gas can be reduced to 5 ppm or below. Moreover, by using the heat-treated active carbon in combination with conventional denitration based on selective catalytic reduction, the nitrogen oxide concentration in exhaust gas can be reduced to 1 ppm or below.

FIG. 1


1
2
3
4
5
6
BOILER
DENI-
TRATOR
AIR
PRE-
HEATER
DUST
COLLEC-
TOR
GAS-
GAS
HEATER
DESUL-
FURIZER
STACK
7

F I G. 2

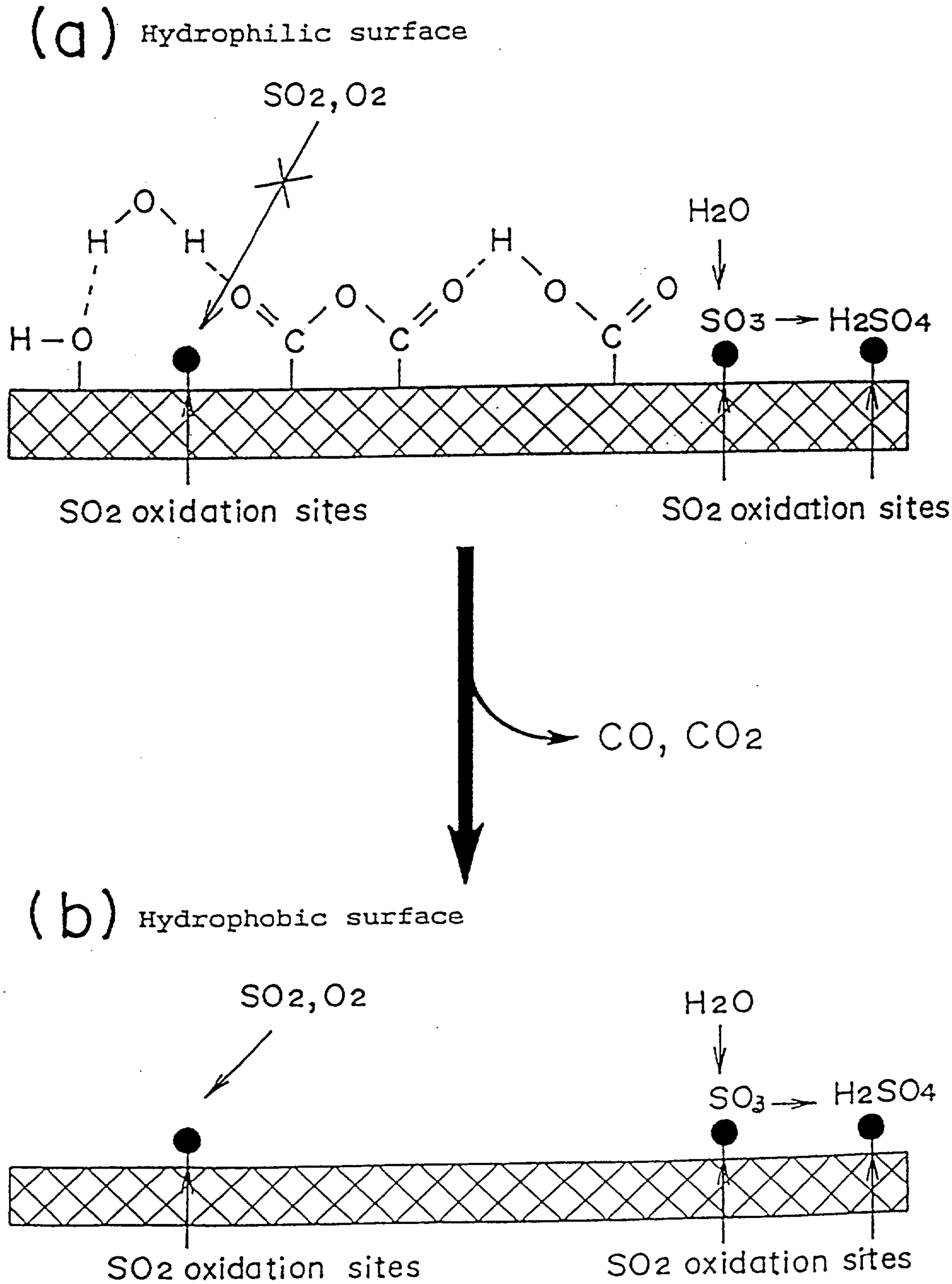

(a) Hydrophilic surface
SO2, O2
H2O
SO3 → H2SO4
SO2 oxidation sites
SO2 oxidation sites
CO, CO2
(b) Hydrophobic surface
SO2, O2
H2O
SO3 → H2SO4
SO2 oxidation sites
SO2 oxidation sites

FIG. 3

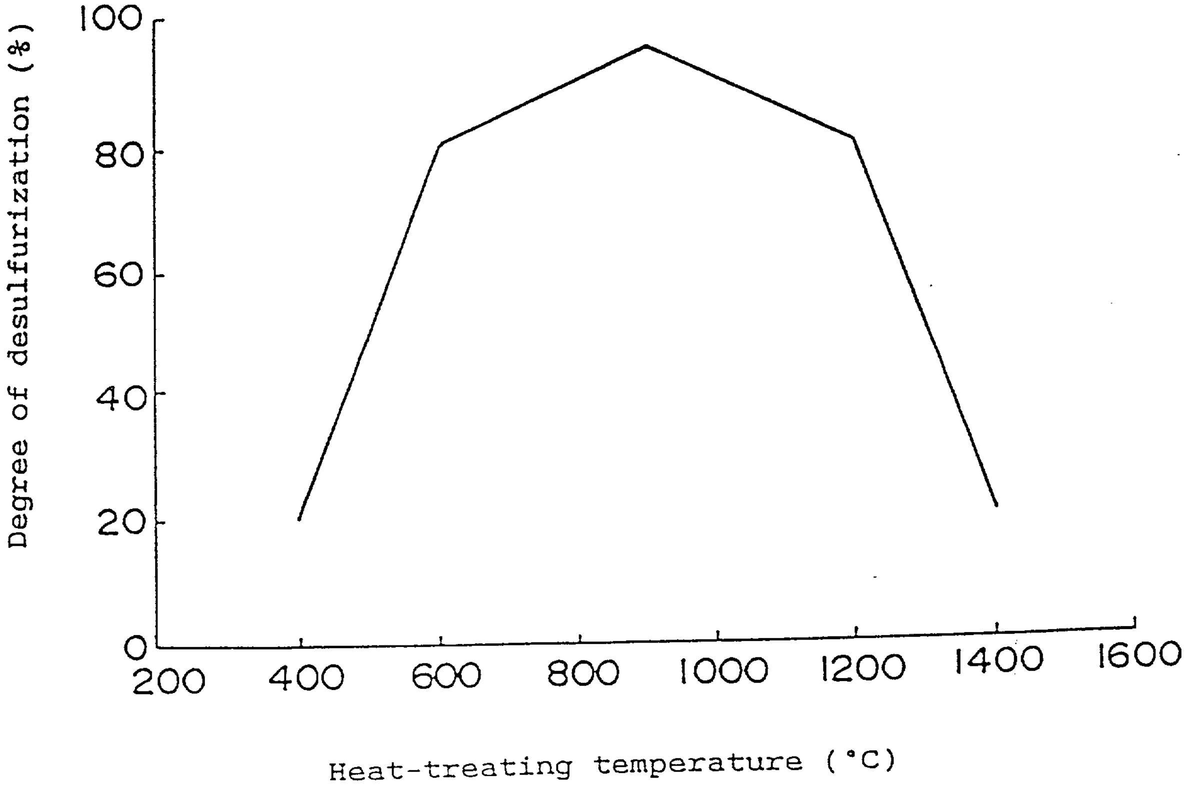
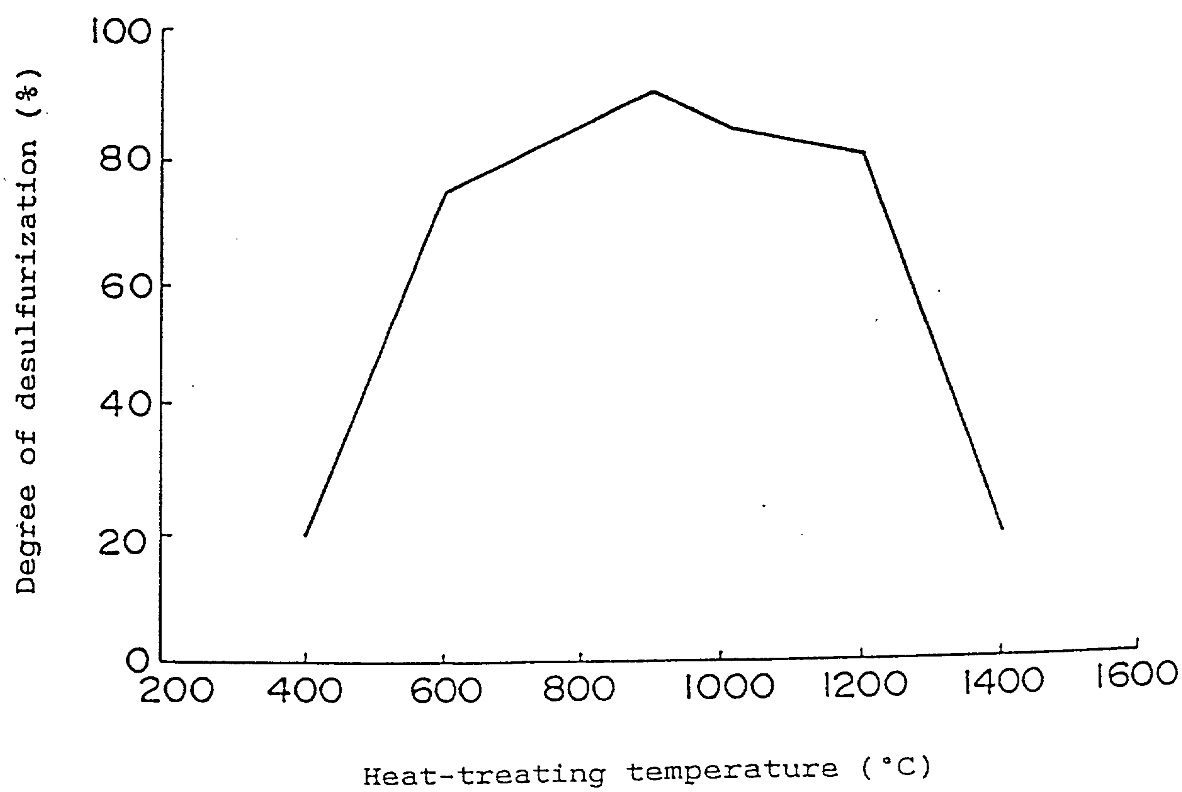
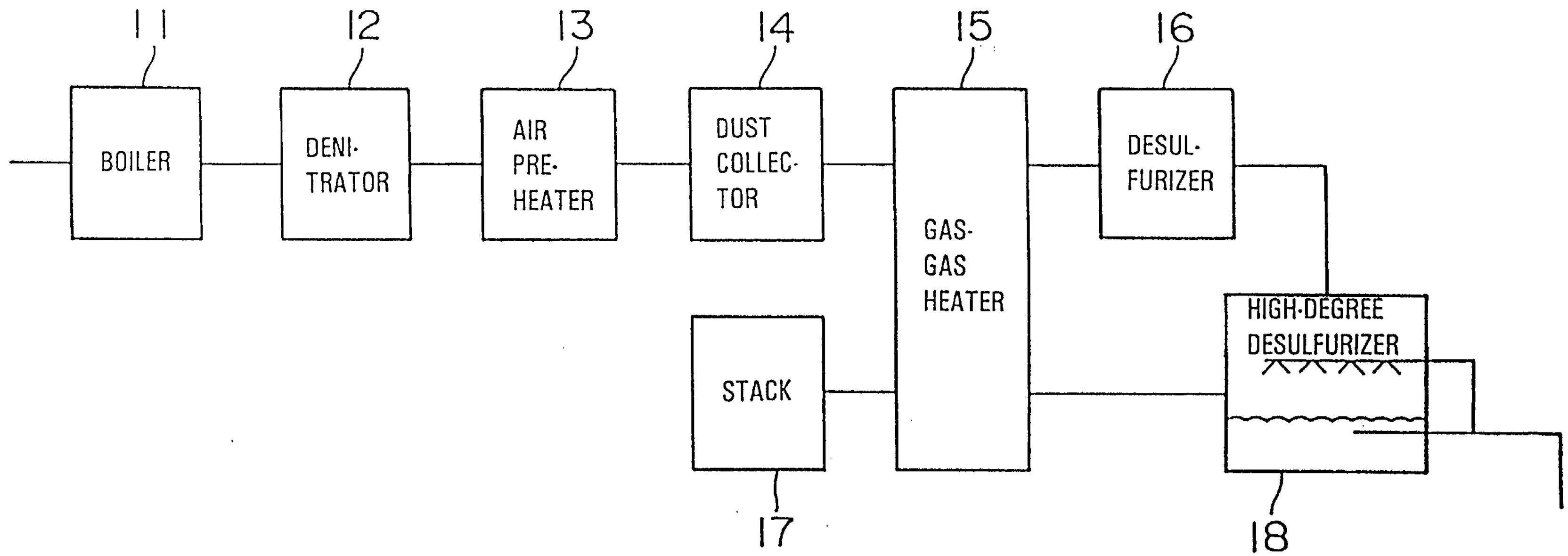

Degree of desulfurization (%)
100
80
60
40
20
0
200
400
600
800
1000
1200
1400
1600
Heat-treating temperature (°C)

FIG. 4



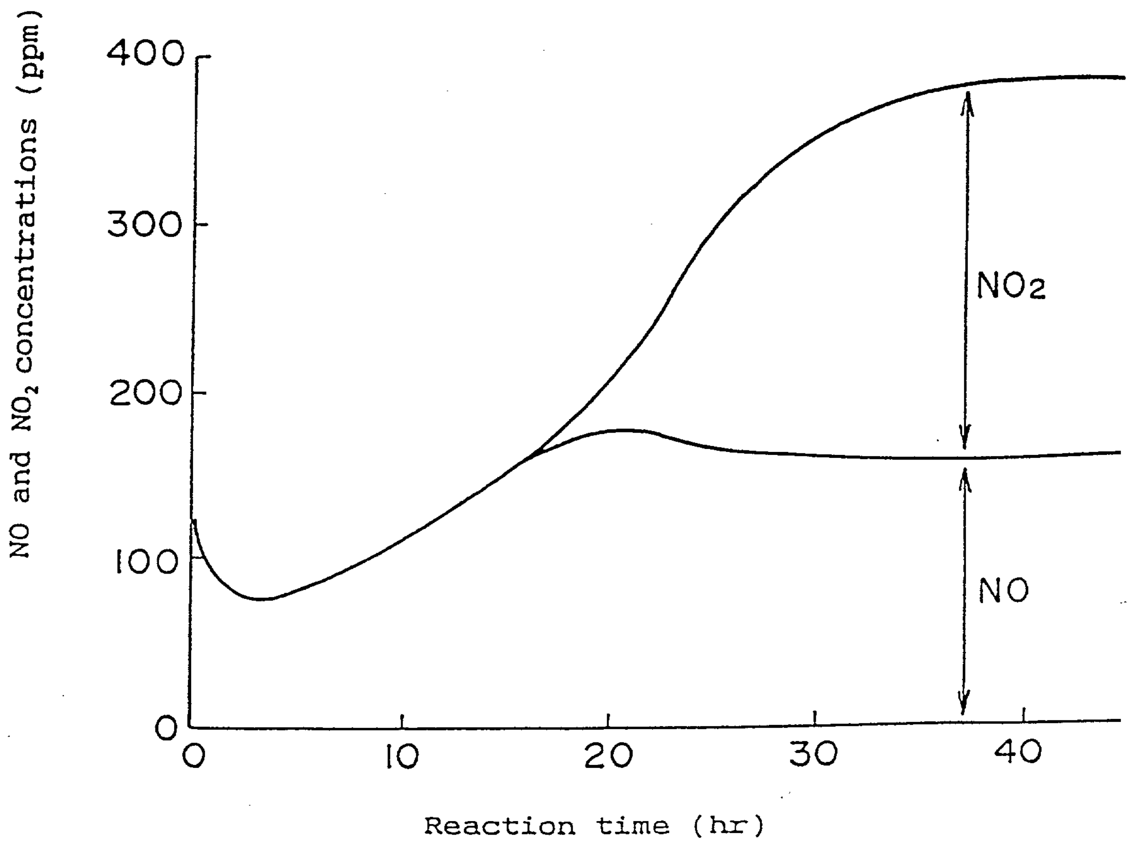
100
80
60
40
20
0
200
400
600
800
1000
1200
1400
1600
Degree of desulfurization (%)
Heat-treating temperature (°C)

FIG. 5



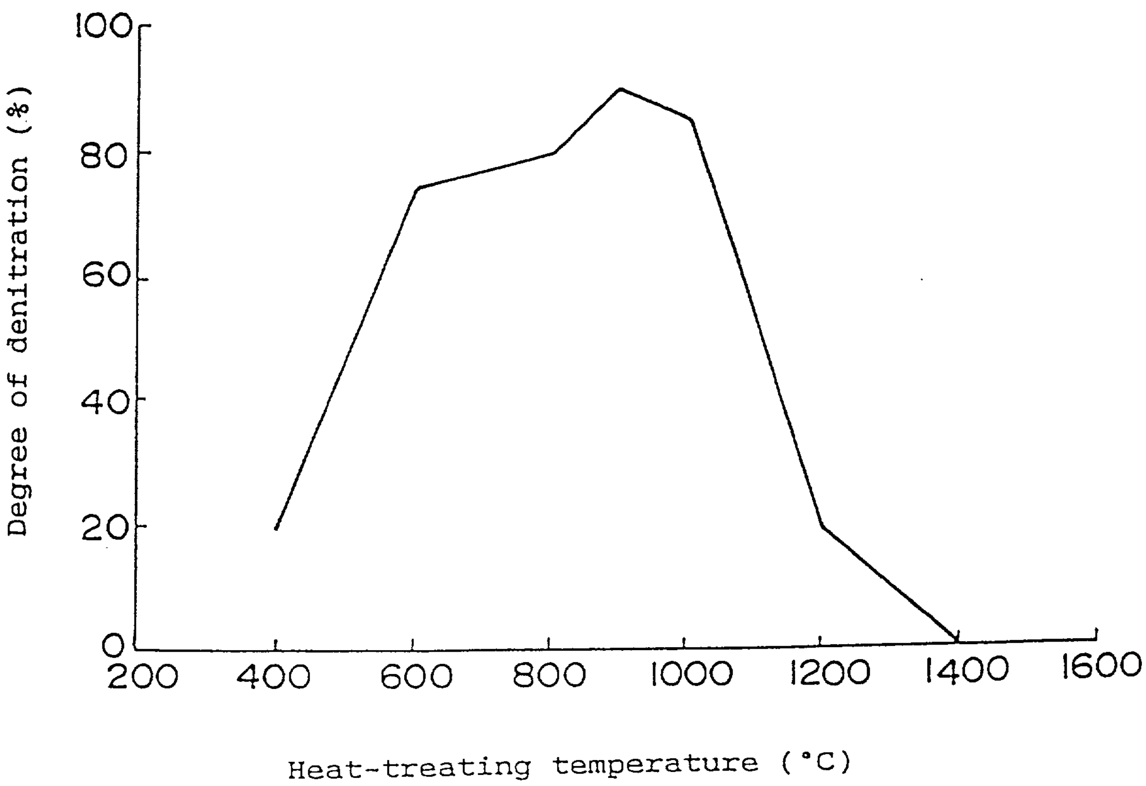
11
BOILER
12
DENI-
TRATOR
13
AIR
PRE-
HEATER
14
DUST
COLLEC-
TOR
15
GAS-
GAS
HEATER
16
DESUL-
FURIZER
STACK
17
HIGH-DEGREE
DESULFURIZER
18

FIG. 6



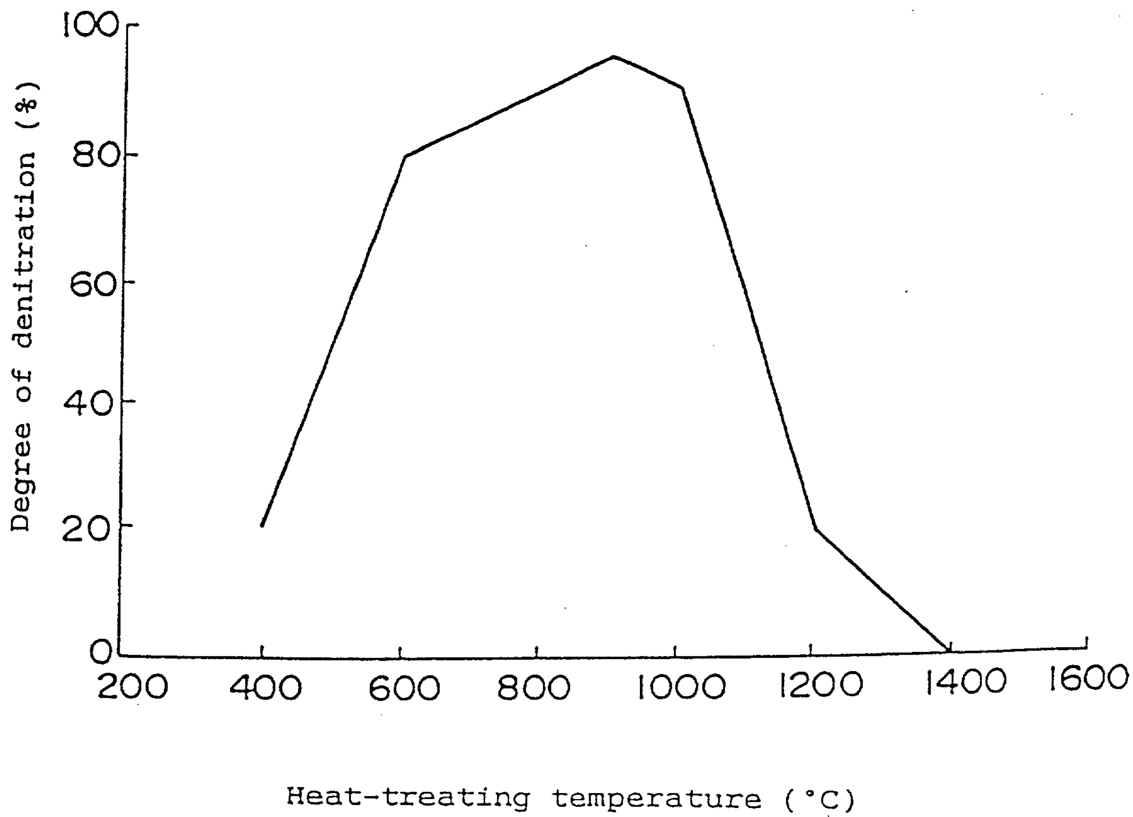
NO and NO_2 concentrations (ppm)
400
300
200
100
0
0
10
20
30
40
NO_2
NO
Reaction time (hr)

FIG. 7



Degree of denitration (%)
100
80
60
40
20
0
200
400
600
800
1000
1200
1400
1600
Heat-treating temperature (°C)

FIG. 8



100
80
60
40
20
0
Degree of denitration (%)
200
400
600
800
1000
1200
1400
1600
Heat-treating temperature (°C)

09/230,600 dotted header number rendered; see note

FIG. 9

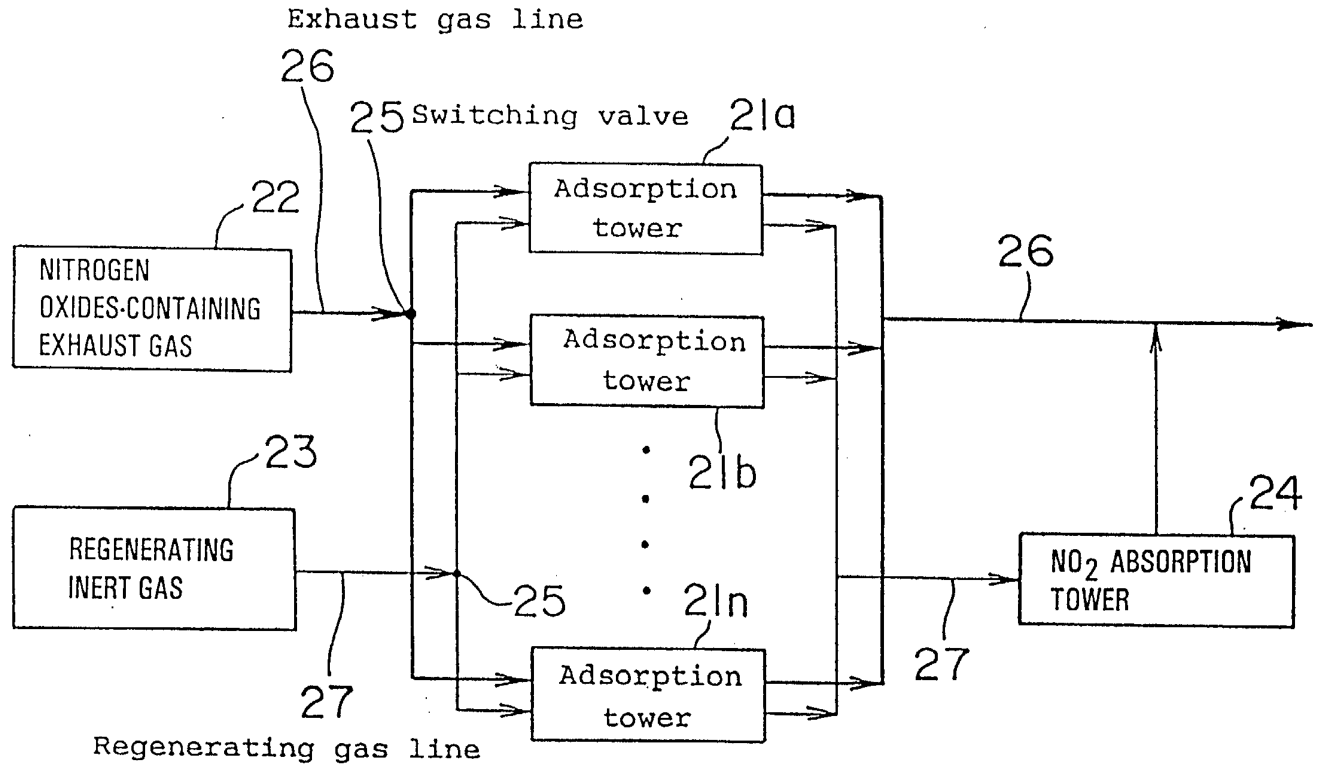
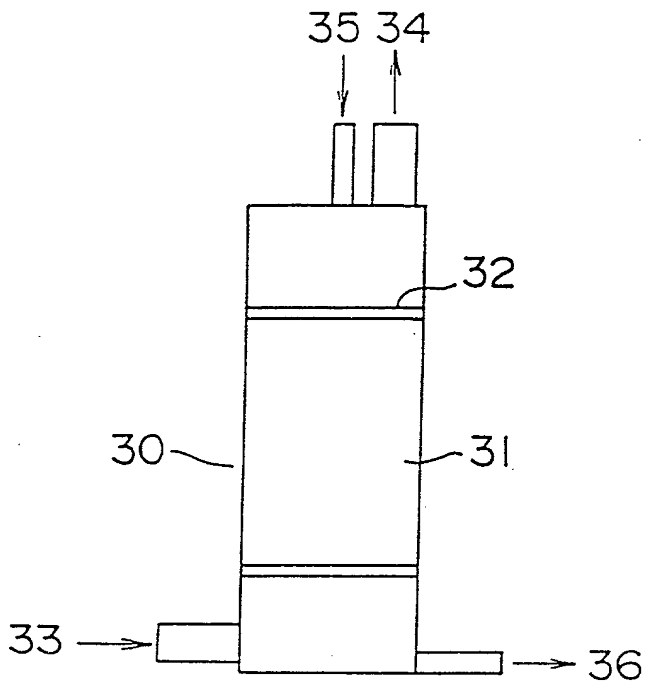
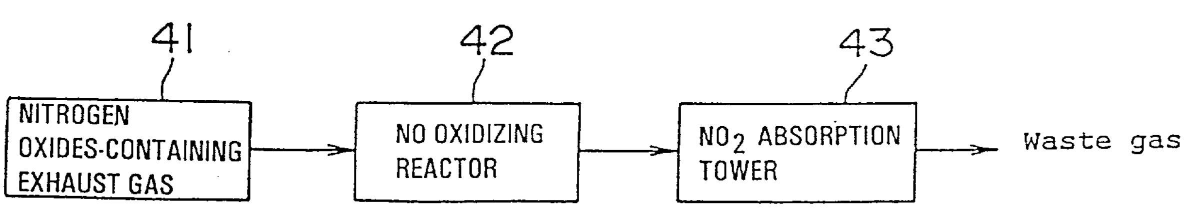


FIG. 10



35
34
32
30
31
33
36

FIG. 11



41
42
43
NITROGEN OXIDES-CONTAINING EXHAUST GAS
NO OXIDIZING REACTOR
NO_2 ABSORPTION TOWER
Waste gas

F I G. 12

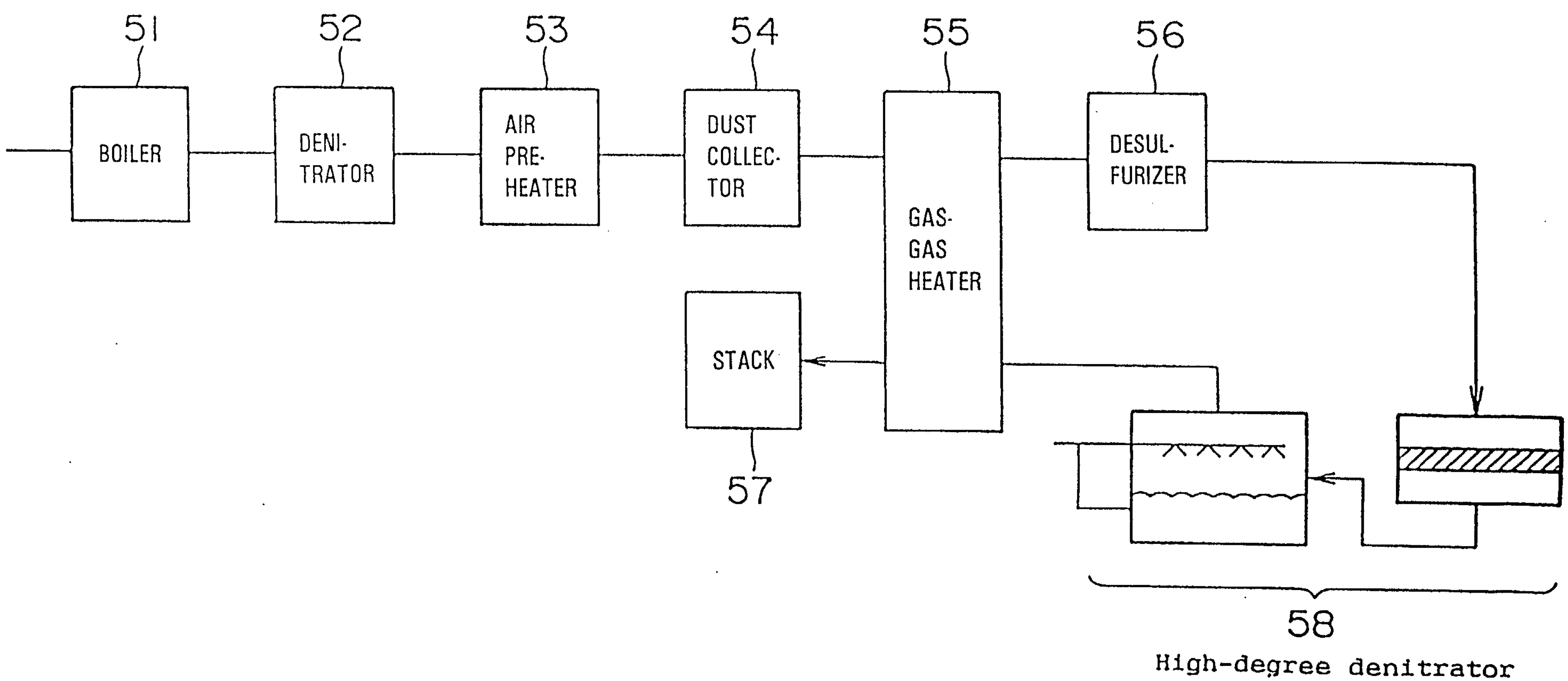
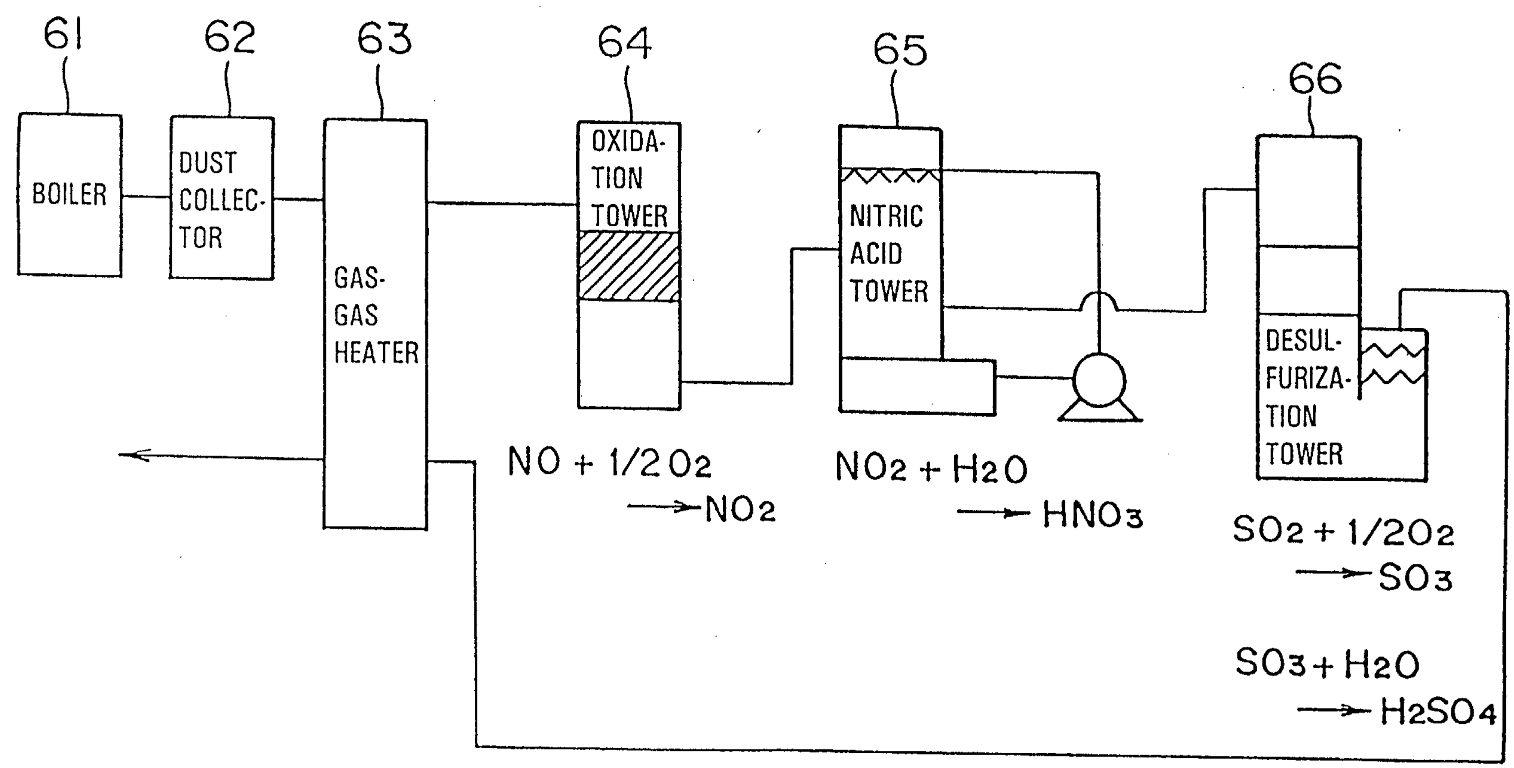

51
BOILER
52
DENI-
TRATOR
53
AIR
PRE-
HEATER
54
DUST
COLLEC-
TOR
55
GAS-
GAS
HEATER
56
DESUL-
FURIZER
STACK
57
58
High-degree denitrator

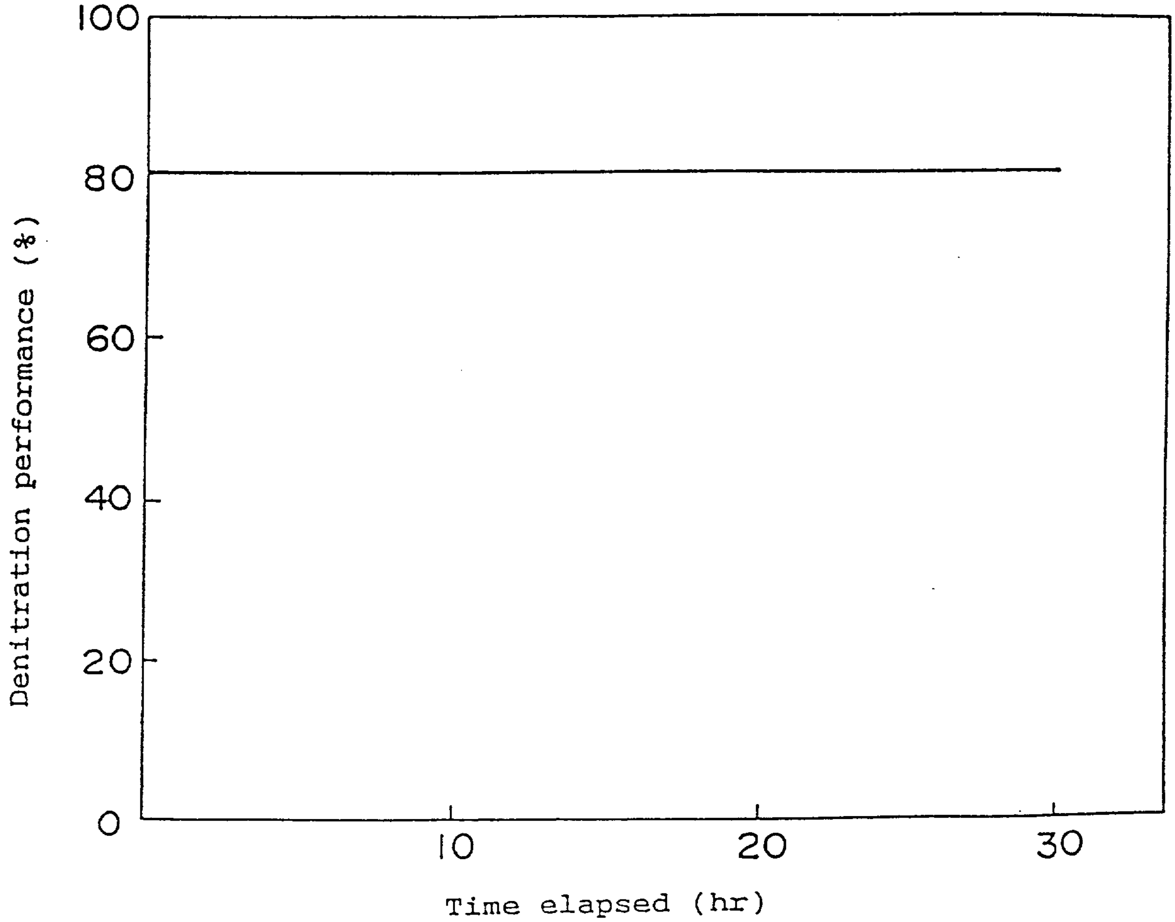
FIG. 13



61
62
63
64
65
66
BOILER
DUST COLLEC-TOR
GAS-GAS HEATER
OXIDA-TION TOWER
NITRIC ACID TOWER
DESUL-FURIZA-TION TOWER
$NO + 1/2O_2 \rightarrow NO_2$
$NO_2 + H_2O \rightarrow HNO_3$
$SO_2 + 1/2O_2 \rightarrow SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$

FIG. 14

Performance on the Oxidation of NO to NO_2



(Conditions)

Temperature of the gas to be treated: 25°C

Composition of the gas to be treated:

NO: 380 ppm

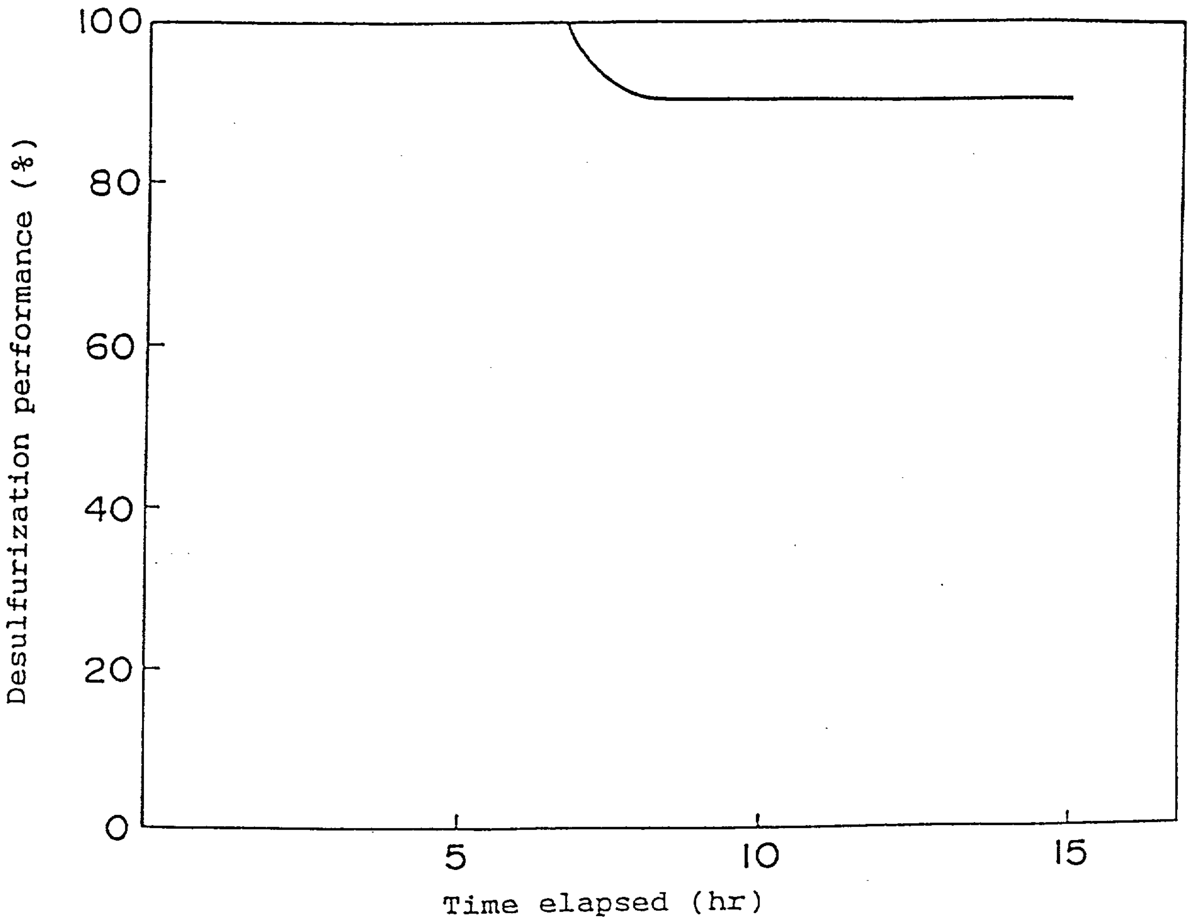
O_2: 4.0%

H_2O: Relative humidity 60%

$W/F = 1 \times 10^{-2}$ g·min/ml

FIG. 15

Performance on the Oxidation of SO_2 to SO_3



(Conditions)

Temperature of the gas to be treated: 30°C

Composition of the gas to be treated:

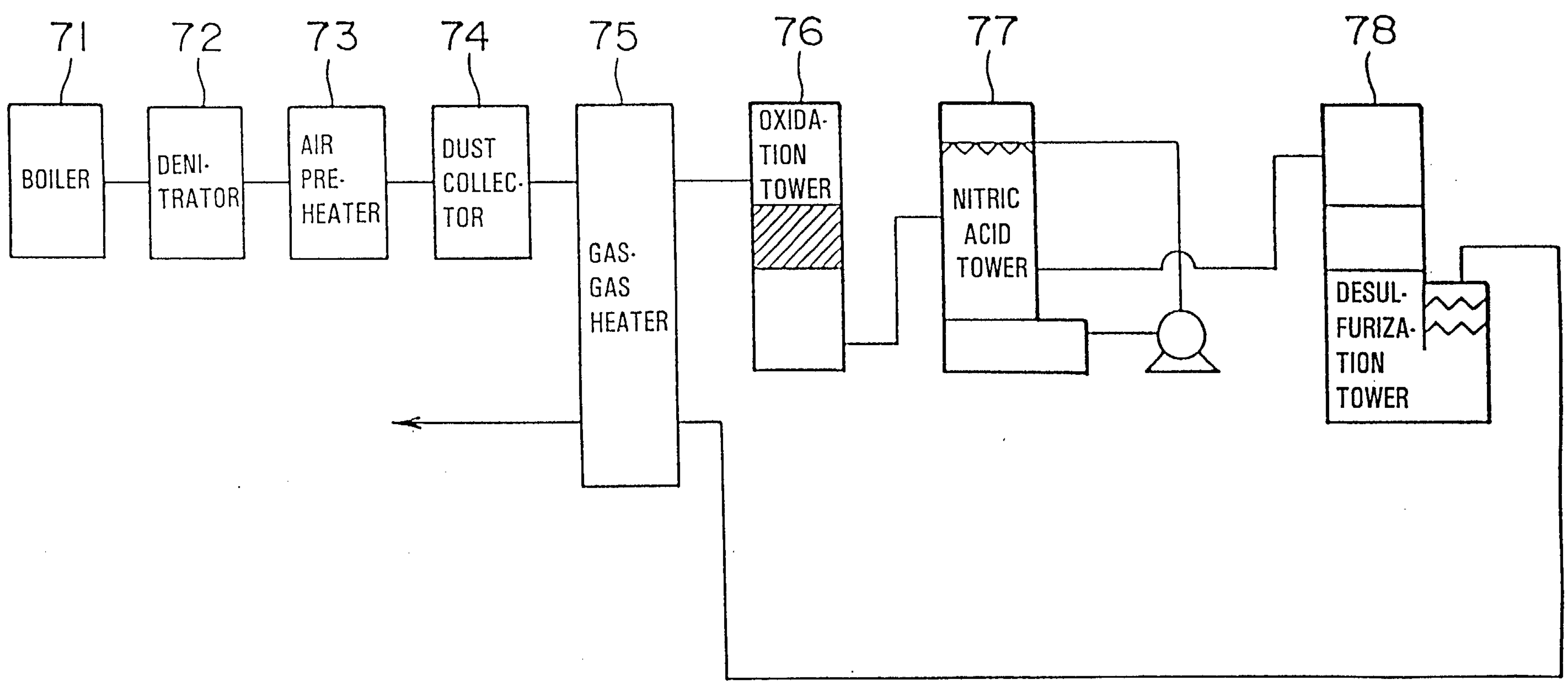
SO_2: 500 ppm

O_2: 5 vol.%

H_2O: 10 vol.%

W/F = 5.0×10^{-4} g·min/ml (W/F is a value obtained by dividing the amount of active carbon fiber packed by the flow rate of the gas to be treated.)

F I G. 16


71
72
73
74
75
76
77
78
BOILER
DENI-
TRATOR
AIR
PRE-
HEATER
DUST
COLLEC-
TOR
GAS-
GAS
HEATER
OXIDA-
TION
TOWER
NITRIC
ACID
TOWER
DESUL-
FURIZA-
TION
TOWER

F I G. 17

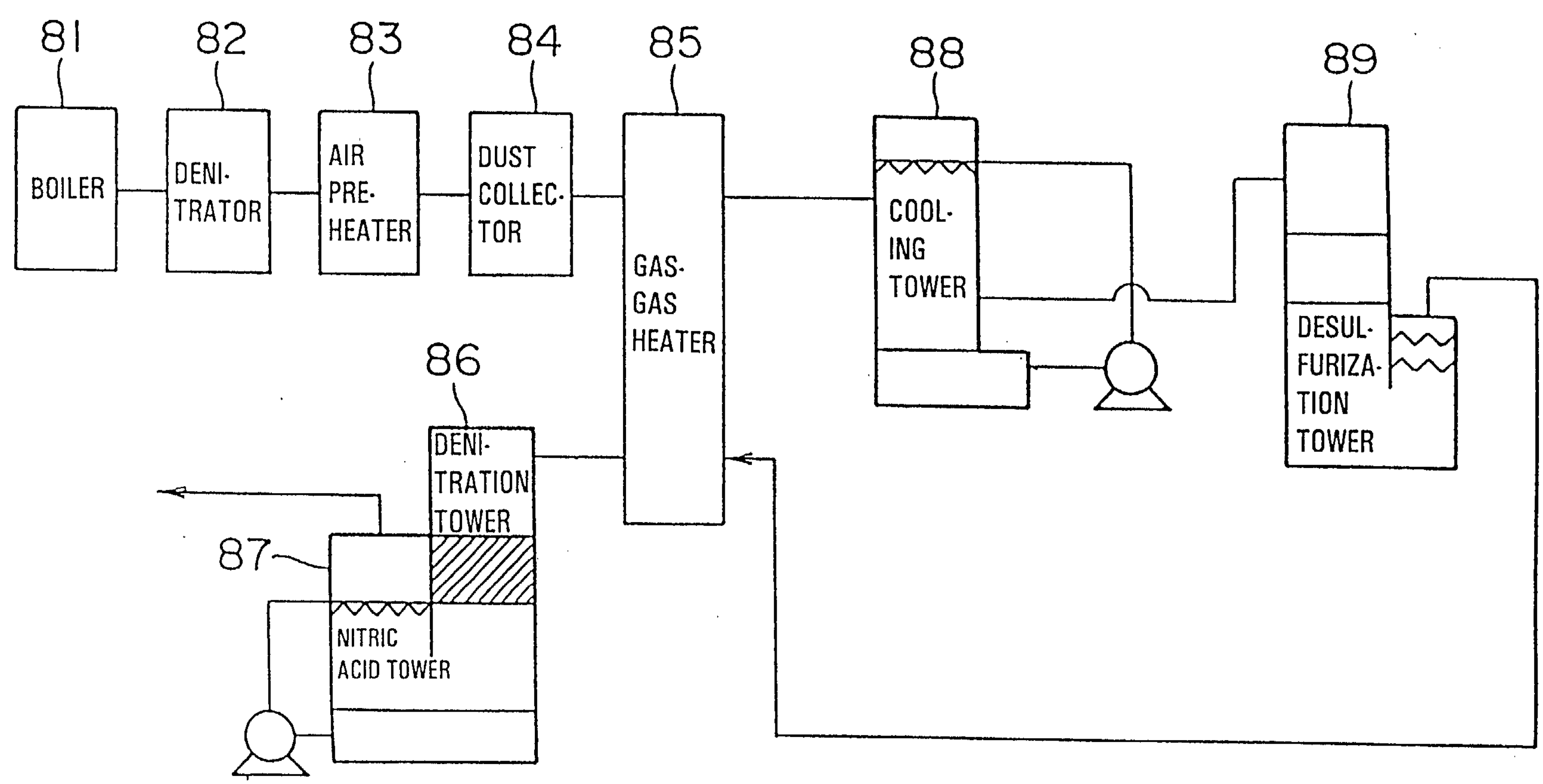
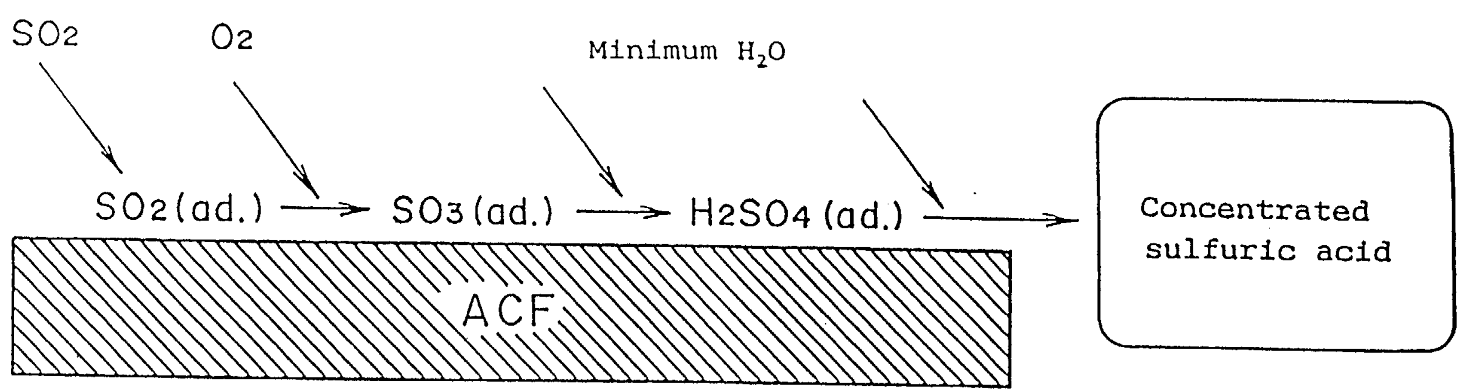

81
82
83
84
85
86
87
88
89
BOILER
DENI-
TRATOR
AIR
PRE-
HEATER
DUST
COLLEC-
TOR
GAS-
GAS
HEATER
DENI-
TRATION
TOWER
NITRIC
ACID TOWER
COOL-
ING
TOWER
DESUL-
FURIZA-
TION
TOWER

FIG. 18


SO2
O2
Minimum H2O
SO2(ad.)
SO3(ad.)
H2SO4(ad.)
ACF
Concentrated sulfuric acid

Docket No. ____________

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

EXHAUST GAS TREATING SYSTEMS

the specification of which (check one)

☐ is attached hereto

☒ was filed on June 27, 1996 as Application Serial No. PCT/JP96/01772 and was amended on ____________ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known by me to be material to patentability as defined in Title 37, Code of Federal Regulations § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

NUMBER	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
162650/1995	Japan	28/June/1995	Yes
268296/1995	Japan	17/October/1995	Yes
272280/1995	Japan	20/October/1995	Yes
285664/1995	Japan	2/November/1995	Yes
285666/1995	Japan	2/November/1995	Yes

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is known by me to be material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION SERIAL NO.	FILING DATE	STATUS: PATENTED, PENDING, ABANDONED
[illegible]	[illegible]	[illegible]

I hereby appoint as my attorneys, with full powers of substitution and revocation, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Stephen A. Bent, Reg. No. 29,768; David A. Blumenthal, Reg. No. 26,257; John J. Feldhaus, Reg. No. 28,822; Donald D. Jeffery, Reg. No. 19,980; Peter G. Mack, Reg. No. 26,001; Brian J. McNamara, Reg. No. 32,789; Sybil Meloy, Reg. No. 22,749; Colin G. Sandercock, Reg. No. 31,298; Bernhard D. Saxe, Reg. No. 28,665; Richard L. Schwaab, Reg. No. 25,479; Arthur Schwartz, Reg. No. 22,115.

Send all correspondence to *FOLEY & LARDNER*, 3000 K Street, N.W., Suite 500, P.O. Box 25696, Washington, DC 20007-8696.
Address telephone communications to *Bernhard D. Saxe* at (202) 672-5300.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of First or Sole Inventor	Signature of First or Sole Inventor	Date
Isao MOCHIDA	Isao Mochida	December 1996

Residence Address	Country of Citizenship
Fukuoka-ken, Japan	Japan

Post Office Address
28-10, Kashii 2-chome, Higashi-ku, Fukuoka-shi, Fukuoka-ken 813, Japan

Signatures should conform to names as typewritten. ☐ Additional inventors on attached Page 2.

DECLA..ATION AND POWER O. ATTORNEY

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Full Name of First or Sole Inventor	Signature of First or Sole Inventor	Date
Akinori YASUTAKE	Akinori Yasutake	December 1996
Residence Address	**Country of Citizenship**	
Nagasaki-ken, Japan	Japan	
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Signatures should conform to names as typewritten. ☒ Additional inventors on attached Page 2.

Docket No.

Full Name of Second Inventor	Signature of Second Inventor	Date
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Residence Address	Country of Citizenship
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Post Office Address c/o Nagasaki Research & Development Center, MITSUBISHI JUKOGYO KABUSHIK KAISHA, 717-1, Fukahori-machi 5-chome, Nagasaki-shi, Nagasaki-ken 851-03, Japan

Full Name of Third Inventor	Signature of Third Inventor	Date
Norihisa KOBAYASHI	Norihisa Kobayashi	December 5, 1996

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Full Name of Fourth Inventor	Signature of Fourth Inventor	Date

Residence Address	Country of Citizenship

Post Office Address

Full Name of Fifth Inventor	Signature of Fifth Inventor	Date

Residence Address	Country of Citizenship

Post Office Address

Full Name of Sixth Inventor	Signature of Sixth Inventor	Date

Residence Address	Country of Citizenship

Post Office Address

Full Name of Seventh Inventor	Signature of Seventh Inventor	Date

Residence Address	Country of Citizenship

Post Office Address

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My residence, post office address, and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names ar listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

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Full Name of First or Sole Inventor	Signature of First or Sole Inventor	Date
Takahiro KASUH	Takahiro Kasuh	December 1996
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Signatures should conform to names as typewritten. ☒ Additional inventors on attached Page 2.

Docket No.__________

Full Name of Second Inventor	Signature of Second Inventor	Date
Masaaki YOSHIKAWA	M. Yoshikawa	December 5 1996
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Post Office Address		
c/o OSAKA GAS COMPANY LIMITED, 1-2, Hiranomachi 4-chome, Chuo-ku, Osaka-shi, Osaka-fu 541, Japan		

Full Name of Third Inventor	Signature of Third Inventor	Date
Residence Address	**Country of Citizenship**	
Post Office Address		

Full Name of Fourth Inventor	Signature of Fourth Inventor	Date
Residence Address	**Country of Citizenship**	
Post Office Address		

Full Name of Fifth Inventor	Signature of Fifth Inventor	Date
Residence Address	**Country of Citizenship**	
Post Office Address		

Full Name of Sixth Inventor	Signature of Sixth Inventor	Date
Residence Address	**Country of Citizenship**	
Post Office Address		

Full Name of Seventh Inventor	Signature of Seventh Inventor	Date
Residence Address	**Country of Citizenship**	
Post Office Address		